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![Los Alamos National Laboratory]

A System Engineering Approach in the Analysis of Ionic Liquids Properties

A Dissertation

Submitted to

The School of Graduate and Professional Studies

Department of Computer and Information Systems Engineering

Tennessee State University

In Partial Fulfillment

of the Requirements for the Degree of

Doctor of Philosophy in

Computer Information and Systems Engineering

Jonathan Reynolds

May 2022

IONIC LIQUID ANALYSIS

To the Graduate School:

We are submitting a dissertation by Jonathan Reynolds entitled, *A System Engineering Approach in the Analysis of Ionic Liquids.* We recommend that it be accepted in partial fulfillment of the requirements for the degree, Doctor of Science in Computer Information and Systems Engineering.

Charles McCurry, Ph.D.
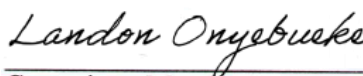
Chairperson
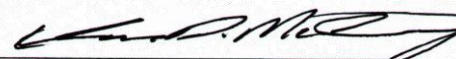
Lizhi Ouyang, Ph.D.

Committee Member

Dr. Landon Onyebueke, Ph.D.

Committee Member

Lee Keel, Ph.D.

Committee Member

Accepted for the Graduate School:

Robbie K. Melton, Ph.D.
Dean of Graduate School

Dedication

I want to dedicate this first to God. Without trusting in Him I don't think I would have made it.

Secondly, I would like to dedicate this to my family. I am grateful for their support. Third I

would like to thank my fiancé Martica Davis, whom when times became dark in this process, she

was there to have my back. I would also like to thank Leatrice Allen her help with my anxiety

has been such a boon to me finishing this process. Lastly to my friends who are my extended

family. I love you and thank you.

JMR

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Abstract

Room temperature ionic liquids (RTIL) are ionic compounds, comprised of a cation and anion, in the liquid state at temperatures below 100 ºC. There are estimated 10^{18} anion and cation combinations, which can create RTILs with unique properties. While the ionic character of RTILs made them attractive in a wide variety of electrochemical applications, their behaviors under electrochemical conditions are not well understood. In this research, we developed a RTIL testbed to investigate how RTILs differ from molecular solvents and electrolytes in electrochemical systems through the study of the effects of their morphology and chemical properties on the electron transfer processes. The test bed is composed of three modules: Electrochemistry, Material characterization, Computational. All modules have been completely developed, verified, and integrated and two of them, i.e., Electrochemistry and Material characterization have been validated in this dissertation. To evaluate the proposed system, experiments were performed on solutions of a redox active species in RTILs. It was found that it is possible to investigate the RTIL's morphology and chemical properties' impact on the electron transfer processes of the solute based on the outcomes and evaluations of tests performed by the RTIL testbed.

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Chapter 1: Concept Stage

The concept stage is the first stage of the generic system life cycle model. The generic system life cycle model is a set of stages, where within system engineers perform technical and management activities. The systems engineering activities in this chapter begin with the identification of need or opportunity for a system. A background review defines the problem space. From the problem space, the engineer develops a problem statement along with the research goal and objectives. The system engineer identifies a system of interest (SOI), and they discuss the feasibility of implementing the SOI. This chapter will also include a discussion of the systems engineering management plan for the SOI.

A. Business/Mission Analysis

In this section, the system engineer identifies the business, mission need, or opportunity. Here the identification; problem background review and definition; research goal, objectives, and system of interest identification; and the SOI technology feasibility analysis will be defined.

1. Need Identification

Room temperature ionic liquids (RTILs) are ionic compounds (organic salts), consisting of a cation and anion, which are in the liquid state at temperatures below 100 ºC. There are many combinations of cations and anions, resulting in approximately 10^{18} possible RTILs. In addition to their unique physical properties, such as negligible vapor pressure, electrical (ionic) conductivity, low toxicity, and high chemical and thermal stability, RTILs can dissolve a wide range of organic and inorganic compounds providing a useful alternative to volatile organic solvents in chemical technologies [1]. Moreover, depending on the cation-anion combination, RTIL properties can be almost freely adjusted to satisfy the demands of many chemical technologies. Understandably, most of the current research focuses on utilizing the unique

chemical and physical properties of RTILs in chemical technologies. The electrical conductivity of RTILs makes them particularly attractive for electrochemical applications, such as lithium-ion batteries and electrodeposition of various metals. However, there are many poorly understood aspects of the behavior of RTILs that require investigation for utilization in such technologies. Among the poorly understood features of RTILs are the speciation of solute ions, dielectric properties, ion association and its effects on thermodynamic and transport properties, and interactions of ionic liquids with solutes, the structure of the interfaces formed between electrodes and ionic liquids [2]. The lack of understanding creates the need to engineer a process to systematically investigate the effects of physical and chemical properties of ionic liquids on elementary electrochemical phenomena, e.g., an electron transfer.

2. Problem Background Review and Definition

Room-temperature ionic liquids are compounds utilized in many different applications due to their unique attributes. One attribute that stands out is their ability to function as both a solvent and electrolyte. In classical electrochemistry, these two roles are fulfilled by two separate substances whose individual effects on electrochemical processes are quite well understood. Scientists and engineers have used this knowledge to create electrochemical devices such as lithium-ion batteries and fuel cells. These systems use the electrochemical charge transfer phenomenon to produce energy. An electron transfer is the most straightforward electrochemical charge transfer phenomenon, whose activation energy and reaction rate are predominantly affected by the solvent. Since molecular solvents are continuous isotropic phases, their effects on charge transfer phenomena can be associated with their macroscopic properties. For instance, Marcus theory correlates the rate of electron transfer reaction with the dielectric permittivity of the molecular solvent and its refractive index [3]. In ionic liquids, on the other hand, there are

well defined microscopic domains with entirely different properties from each other and molecular solvents. The sizes and shapes of these domains are determined by individual properties of ions, such as their charge, charge location, size, hydrophobicity/hydrophilicity of their different fragments, their ability to assume different configurations, etc. As a result, every ionic liquid has its unique morphology. That morphology determines the immediate environment of a solute undergoing an electron transfer reaction in an ionic liquid. While an electron transfer reaction in a molecular solvent requires a reorganization of solvent electrical dipoles, which correlates with the dielectric solvent properties, ions must rearrange in ionic liquids for an electron transfer reaction to occur. However, there is no clear understanding of how the morphology of ionic liquids affects electron transfer reactions.

3. **Research Goal, Objectives, and System of Interest Identification**

The goal of this project is to investigate the RTIL's morphology and chemical properties' impact on the electron transfer processes of simple inorganic ions. The system of interest (SOI) in this research effort is a testbed to study the morphology of ionic liquids affecting electron transfer reactions. The SOI, shown in Figure 1, has three modules: electrochemistry, computational, and material characterization.
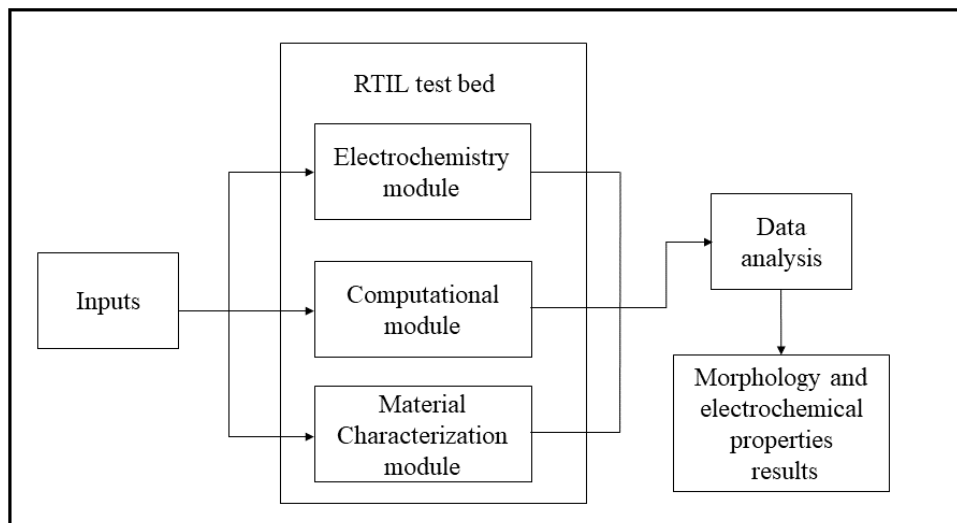
Figure 1. General System of interest

The research objectives are as follows:

1. Develop an electrochemical module that uses standard electrochemical characterization techniques to determine the electrochemical behavior of a model electrochemical system, including its charge transfer kinetics and diffusion coefficients.

2. Development of a computational module that will provide information on the details of RTIL morphology in the absence and presence of a model electrochemical system not accessible by other means, such as the mutual orientation of neighboring ions/ion fragments.

3. Development of a material characterization module that will supply pertinent data on the material properties, such as its microscopic structure and viscosity.

4. Development of the performance evaluation metrics for each module.

5. Testing of the SOI with mixtures of hydrophobic and hydrophilic ionic liquids.

6. Evaluate the results through data analysis to explain the morphology and chemical properties' impact on the electron transfer processes of simple inorganic ions.

4. System of Interest Technology Feasibility Analysis

In this section, we discuss the existence of technologies or methods for the development of the SOI. For the electrochemistry module, technologies are well defined. The primary tool utilized is a potentiostat/galvanostat. They are commercially available from companies such as Gamry and Pine. In addition to the potentiostat/galvanostat, there are also components, such as electrodes and electrochemical cells, which are commercially available or can be self-fabricated that are essential to testing. Commercial software is also available to analyze data, e.g., COMSOL. The computational module is compatible with various computer platforms. There are several molecular dynamics programs such as Siesta and NWChem to run the simulations. The material characterization aspect of the SOI can employ several technologies such as a viscometer and an X-ray diffractometer to determine the viscosity and microscopic ordering of RTILs, respectively.

B. System Engineering Management Plan (SEMP)

The System Engineering Management Plan (SEMP) describes the SE processes for the life cycle stages. The SEMP also explains the manner at which the SOI conducts and manages SE efforts. This SEMP includes tailored activities defining the project scope; roles and responsibilities of the team members; and identifies the support and resources needed to complete the project, assumptions, and constraints. This SEMP culminates with the development of the work breakdown schedule.

1. Project Scope and Constraints:

The project scope is to employ the systems engineering approach to design, develop, and implement a solution to the need explained in this chapter. Tennessee State University and Los Alamos National Laboratory (LANL) facilities have the necessary tools available to facilitate the completion of this project. The testbed will be designed so that it will be fully operational at

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both locations.

2. Roles and Responsibilities:

The member of the SE team is Jonathan Reynolds. He is the process engineer representative. He will be responsible for completing the life cycle process activities along with performing the research for the process. The research advisor is the first point of contact for the team. The department head is above the research advisors in the organization hierarchy. The department head handles conflicts that cannot be resolved by the graduate professor. The chain of command addresses the disputes that cannot be managed by the department head. The chain of command from there is the Assistant Dean of Engineering, the Dean of Engineering, and finally the School of Graduate studies. Figure 2 shows the research hierarchy.
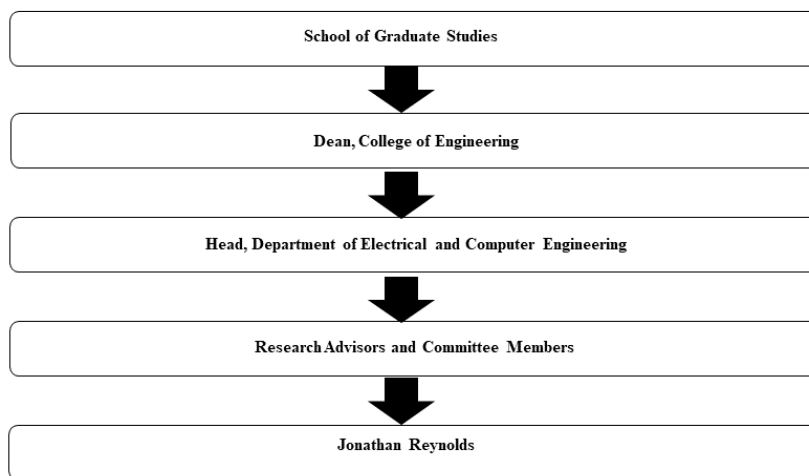
Figure 2. Research Hierarchy

3. Support and Resource Management:

Implementation of the projects' tasks will be at LANL and/or Tennessee State Univ. Training must be completed before work can begin. LANL will provide access to supplies and

equipment to conduct the research. Tennessee State University will also provide access to supplies, equipment, and their computer servers.

4. Process and Activities Scheduling:

SEMP provides knowledge on implementing the systems engineering design process as an organized schedule. Additional time is given for processes to account for any problems that may occur. At the end of each process, either the project moves forward or returns to a previous process to follow the project plan. Table 1 presents the work breakdown schedule in a graphical form. It shows the process activities, the duration of each activity, and when a decision must be made. It is important to remember this schedule is flexible e because some processes completion time may vary.

Table 1. Work Breakdown Schedule

SE Process activities ►represents decision gates	Stage	Activities for 44 weeks (1–44)
Need Identification	Conceptual Stage	weeks 1–3 (▶)
Problem Background Review and Definition	Conceptual Stage	weeks 3–4 (▶)
Research Goal, Objectives, and System of Interest Identification	Conceptual Stage	weeks 4–5 (▶)
System of Interest Technology Feasibility Analysis	Conceptual Stage	weeks 5–6 (▶)
Needs Identification	Development Stage	weeks 6–7 (▶)
Stakeholder and Requirements Definition	Development Stage	weeks 7–8 (▶)
Alternative Technical Approach Definition & Approach Section	Development Stage	weeks 8–9 (▶)
Literature Review	Development Stage	weeks 9–10 (▶)
Alternative Solutions Election	Development Stage	weeks 10–11 (▶)
Development of Electrochemical Module	Production Stage	weeks 11–18 (▶)
Development of Computational Module	Production Stage	weeks 11–18 (▶)
Development of Material characterization Module	Production Stage	weeks 11–18 (▶)
Integration and Testing of the SOI	Production Stage	weeks 18–27 (▶)
Report Writing	Production Stage	weeks 18–44 (▶)

Chapter 2: Development Stage

The development stage of the system of interest (SOI) includes two sections: A) Requirement's definition and analysis; B) Literature review and technical approach definition. The first section includes the compiling of stakeholder identification, needs and requirements definition; system operational and life cycle concepts; and system requirements definition and analysis. Multiple alternative technical approaches for the system of interest are defined that satisfy the system requirements and a final technical approach selected for the design of the system of interest.

A. Requirement Definition and Analysis

The systems engineering process involves the transformation of stakeholder needs into requirements. In this process, the needs derived from the stakeholders are transformed into requirements to guide the development of the system of interest (SOI). Obtaining the needs of the stakeholders enables the system of interest to provide the capabilities needed by the stakeholders. The stakeholder needs help to develop the stakeholder requirements specification (SRS). This process includes three parts: Stakeholder Identification, Needs and Requirements Definition, System Operational and Life Cycle Concepts, and System Requirements Definition and Analysis.

1. Stakeholder Identification, Needs and Requirements Definition

In the systems engineering approach, a stakeholder is defined as someone who has an interest in the system development. There are two types of stakeholders: major and minor. In this section, the stakeholders are identified for the SOI. Then, the stakeholder needs definition activity is

conducted. Finally, the transformation of stakeholder needs into stakeholder requirements is performed. The SOI stakeholders are shown in Figure 3. The SOI stakeholder are as follows: NNSA-DOE Nuclear Security Enterprise (NNSA): The major stakeholder. With their assistance the system will be tested. They can disseminate the system among its affiliated research organizations to aid electrochemical ionic liquid research.

1. Research institutions: A minor stake holder. They can use the system to further their electrochemical ionic liquid research.

2. Private Industry: A minor stakeholder. They can use the system to further their electrochemical ionic liquid research in their specific electrochemistry technology.
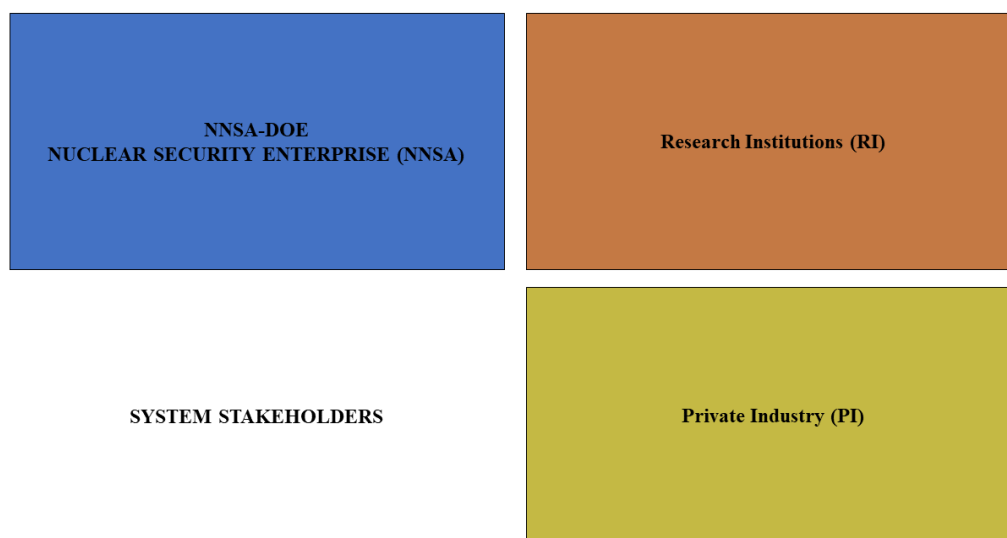
Figure 3. Stakeholders Identification

Table 2. details the needs association, stakeholders, and statements from the stakeholders. As previously mentioned, the stakeholder needs identified above are transformed into system requirements. Therefore, requirements are mapped directly to specific needs.

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Table 2. Stakeholders Need Categorization

Category	Stakeholder Need (Acronyms of stakeholder)
Performance	• I want each module to produce stand alone data. (NNSA, RI) • I want the flexibility to change the tests performed in the electrochemical module as needed (NNSA, RI, PI) • I want the electrochemical module to produce comparable results with comparable inputs no matter the location. (NNSA, RI, PI) • I want the theoretical result to be as accurate as possible. (NNSA, RI, PI)
Utilization	• I want the system to be platform independent. (NNSA, RI, PI) • I want the electrochemical module to be able to be integrated into environmental chambers. (NNSA, RI, PI) • I want the electrochemical module to use standard lab procedures. (NNSA, RI, PI) • I want the system to not require exceptional computational resources. (RI, PI) • I want the electrochemical module to be able to accept non-standard electrodes. (PI, RI) • I want to use any ionic liquid (NNSA, RI, PI) • I want each input to be made as similar as possible (NNSA, RI, PI) • I want the system to work as fast as possible (NNSA, RI, PI) • I want to the system to use minimum physical resources as possible (NNSA, RI, PI) • I want each module to be performed separately (NNSA, RI, PI)

Table 3. represents the stakeholder requirements developed based on the specified needs

for the SOI listed earlier in Table 1. Indeed, stakeholder requirements can be grouped as

performance requirements, environment requirements, utilization requirements, and environment

requirements.

Table 3. Stakeholder Requirements Specification (SyRS)

1.0 Performance Requirements (Per)	
1.1	The system shall output cyclic voltammetry data.
1.2	The system shall output radial distribution functions of the ionic liquids and solute.
1.3	The system shall use output Guinier plots.
1.4	The user shall document each step in the electrochemical module.
1.5	The system shall verify the accuracy of the computational module within ten percent error.
2.0 Utilization Requirements	
2.1	The system shall use potentiostats that can perform impedance and cyclic voltammograms
2.2	The system shall use components that will work in an open laboratory environment or inert environment
2.3	The electrochemical module shall use standard lab techniques that stakeholders can replicate
2.4	The computation module shall not require using more than 32 cores in parallelized molecular dynamic simulation

2. **System Operational and Life Cycle Concepts**

The operational concepts are derived from how the system should function. For this

system, each module has its own operational concepts. For the electrochemical module, the

system can be operated by using standard lab techniques used by governments and institutions.

They can use most potentiostats to perform electrochemistry experiments in a three-electrode

configuration on the selected ionic liquid and solute. The computational module uses standard

molecular dynamic simulation techniques used by governments and individuals. They can use

their chosen computational system to perform molecular dynamic simulation on the selected

ionic liquid and solute using Siesta. For the computational module, the system can be operated

by using standard lab techniques used by governments and institutions. Since most users will

use need to use a user facility, they will have to follow the regulations for that facility. Life cycle

concepts are derived from scenarios relating to a life cycle stage. This section includes a

discussion of the life cycle concept for the SOI with respect to the life cycle stages including the

design and production, the operation, the support, and the retirement. The life cycle concepts are

not discussed in-depth in this report. Therefore, a sample of the life cycle concepts is provided in

Table 4.

Table 4. Life Cycle Stage Concepts

Life Cycle Stage	
Design and Production	- The computational module will utilize a high-performance computing platform provided by TSU. - The system will be tested fully.
Support	In case of the high-performance computing platforms is out of order or fails to function as supposed, it will be replaced by TSU.
Retirement	The system will not have a traditional retirement stage. Since it is a process, each module can be upgraded to fit current trends and use state of the art equipment.

3. **System Requirements Definition and Analysis**

The system requirements are the descriptions of the system services and constraints. They

are developed from several main sources including: the stakeholder needs and requirements, the

system operational concept, and the system life cycle concepts. These system requirements will

provide the capabilities needed of the system of interest. Using these he SOI requirement

specifications were established and are provided in Table 5.

Table 5. System Requirements Specifications (Srys)

	System Requirements
1.1	A manual shall be created to document procedural needs of utilization of the subsystem
1.2	The manual shall facilitate directions for system operation and calibration techniques to anyone with standard lab training
1.3	The system shall be physically adaptable to different test cells and electrochemical analytical techniques
1.4	The system shall be physically adaptable to different test cells and electrochemical analytical techniques
1.5	The system shall output cyclic voltammetry data at a minimum of two scan rates
1.6	The system shall output radial distribution functions of the CU-Cl ion pair
1.7	The system shall output 1D X-ray scattering patterns
1.8	The system shall use Siesta to perform the molecular dynamics simulations
1.9	The system will only be verified for criteria that falls within a 10% error of the expected value

B. Literature Review and Technical Approach Definition

Now that the stakeholders and the system requirements are identified, various technical approaches for the development of the system of interest ought to be identified. Accordingly, several technical approaches for each subsystem development of SOI were picked. Finally, a distinct approach was nominated for each subsystem design.

1. Literature Review

It is uncertain which research group was the first to synthesize a room temperature ionic liquid; several groups have reported about their successes making room-temperature ionic liquids. RTILs have had an impact on various fields of science because of their adaptability to different processes. Their versatility comes from the ability to adjust their properties through the selection of the cations and anions and thus allows them to cater to specific needs. RTILs have

the potential to solve some of the grand engineering challenges by emerging as a clean, efficient, and environmentally friendly alternative to volatile organic solvents [4].

Ionic liquid's (ILs) versatility is their biggest strength, ILs can play a vital role in chemical analysis, e.g., by being the main component in extraction processes. Liquid-liquid extraction is based on the partitioning of the target compound between two immiscible phases, using the distinct phases to extract the target compounds such as metal ions and acids [5]. RTILs have also found applications in sensor technologies. One group reported on the suitability of RTILs as the electrolyte in electrochemical gas sensors. Using RTIL's eliminated the use of a membrane, whose role is to separate the sample from the electrolyte. Such RTIL-based sensors can work in a robust environment [6]. Ionic liquids have the potential to be a new electrolyte media for lithium metal batteries. The breakdown of the electrolyte material in Li-ion batteries is one of the most significant issues that plague the technology. RTILs are a reasonable replacement for the current electrolyte in Li-ion batteries because of their thermal stability and the resistance to electrochemical decomposition [7]. Another use of RTILs taking advantage of their unique properties is as stationary phases in gas chromatography (GC). Researchers synthesized select RTILs and compared them to typical GC stationary methods [8].

ILs are of interest in electrochemistry because of their relatively high ionic conductivity. While the conductivities of ILs are lower than those of conventional electrolyte solutions [9], they are still sufficiently high to perform numerous bulk electrochemical oxidations or reductions. Moreover, many ILs have a wide electrochemical potential window. The large potential window is beneficial for electrochemical work, as this ensures that there is not any breakdown of IL during electrochemical studies and processes[10].

a) *Single Electron Electrode Reactions in Room Temperature Ionic Liquids.*

While the use of ILs in electrochemical processes has been growing each year, there are still physical and chemical unknowns due to the complex nature of the IL or the physical meaning of the reference electrode potential in IL's. Ionic conductivity of ILs, while sufficiently high to guarantee their use as electrolytes in numerous electrochemical processes/devices, is found too low for some other applications. The ohmic drop resulting from the electrical current flow in a medium with insufficient ionic conductivity and the lack of a universal reference electrode makes the comparison of data obtained by different research teams using different ionic liquids rather difficult and the conclusions from such comparisons doubtful [11]. Errors result in the inaccurate reproduction and comparison of the data collected, which makes results from different experiments hard to interpret in the electrochemical community. The potential differences of reference electrodes in ILs are barely studied, preventing proper comparison of potential data measured even among different research groups using the same IL [12]. It is imperative that in electrochemistry research consideration is taken for the type of reference electrode used.

Single-electron transfer (ET) reactions are the simplest charge transfer reactions and have served as model systems in studies of solvent effects on charge transfer phenomena. Those studies shaped the current understanding of the mechanisms and kinetics of ET reactions in molecular solvents [3]. As opposed to such solvents, ILs are composed exclusively of ions and serve as both solvent and electrolyte in ET processes [3]. These differences led to an interest in understanding the fundamental effects governing the electron transfer reaction in these liquids, which are both the electrolyte and solvent. Not many studies of one-electron redox systems in ILs have been devoted to addressing that fundamental difference. Frequently, the specific electrochemical behavior of a one-electron system has been reported because of its practical importance in technology. The following are representative research studies focusing on one

electron reactions in ILs. Dolidze et al. performed high-pressure kinetic studies on electron exchange for two redox reactions, $[Fe(bipy)_3]^{3+/2+}$ and $[Fe(cp)_2]^{+/0}$. They used 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, (BMIM BTA) kept in a nitrogen environment. Through cyclic voltammetry (CV) measurements and simulations of the CV data, they found a correlation between the ET rate constants as well as diffusion coefficients of the solute and the reaction pressure and temperature [13].

Chen et al. studied the electrochemical behavior of the Li^+/Li couple in tri-1-butylmethylammonium bis(trifluoromethylsulfonyl)imide ionic liquid mixed with propylene carbonate [14]. Chen et al. used an electrochemical cell composed of a single compartment with three electrodes. The cell was placed in a glove box filled with dry nitrogen. Chen et al. used four different working electrodes in these experiments, namely a tungsten wire sealed in a Pyrex glass, a Pt wire, and a copper wire sealed in a heat-shrinking Teflon tube and an aluminum rod also sealed in a heat-shrinking Teflon tube. A platinum wire dipped in BMIM Tf_2N ionic liquid in a glass tube with a frit was used as the counter electrode. Lithium cations, whose reduction was studied, were introduced into the liquid as solid $LiTf_2N$. However, they found that the Li metal deposition was progressively inhibited by a side reaction leading to the growth of an interfacial layer of a solid electrolyte. The formation of such layers impedes the application of ILs in lithium batteries, as it quenches the Li^+/Li reactions over time.

Tan et al. investigated the electrochemical behaviors of U(VI) in 1-butyl-3-methylimidazolium chloride (BMIM Cl) with different water contents [15]. Tan et al. used a three-electrode cell, having a Pt wire counter electrode, an Ag wire quasi reference electrode, and a glassy carbon working electrode. The results suggested that U (VI) is irreversibly reduced to U (V) in the BMIM Cl ionic liquid with various amounts of water. Tan el al states that the

reduction of U (VI) to U (V) is controlled by both the diffusion of U species and the charge

transfer kinetics.

Jayachandran et al. studied the electrochemical behavior of NpO_2^+ in 1-Hexyl-3-

methylimidazolium bis(trifluoromethylsulfonyl)imide (HMIM Tf_2N) [16]. In these experiments,

they used a glassy carbon disk working electrode and two Pt wires acting as counter and quasi-

reference electrodes. They indicate that NpO_2^+/ NpO_2^{2+} redox reaction in HMIM Tf_2N is quasi-

reversible. They were able to determine the diffusion coefficient of NpO_2^+ in HMIM Tf_2N.

b) Molecular Dynamic Simulations of Ionic Liquids.

Currently, knowledge on ionic liquids is predominantly empirical. With a detailed

understanding of IL's physicochemical behavior, enhancements of processes can be created. One

way to achieve a desired physicochemical behavior is through modeling and simulations. Popolo

et al. used two molecular dynamics (MD) methods to get information on the internal structure,

the spatial distributions of the ions, etc. of their chosen IL [17]. They used isothermal–isobaric

ensemble to study the structural and thermodynamic properties of the system. They also used a

micro-canonical ensemble to get the dynamics of the system. They found that the internal

structure is influenced by two competing factors: ion packing and charge screening.

Kodderman et al. focused on refining the force field parameters in MD simulations [18]. They

mostly used the statistical ensemble where you have a constant pressure, and constant temperature

(NPT) for their simulation of the parameters they concentrated on, such as the thermodynamic

properties. They used statistical ensemble where you have where you have constant volume and

constant energy (NVE) to get viscosity values. They found that by refining their force field

parameter, they could achieve results similar to experimental data within an acceptable margin of

error.

2. **Alternative Architecture Definitions and Architecture Selection**

Alternative technical approaches presented in this section involve evaluating different considered techniques for developing the elements of the SOI. As mentioned earlier, the SOI in this research composed of three main modules: The electrochemistry module, the computational module, and the material characterization module.

a) *Electrochemistry module.*

As mentioned in the System of Interest Technology Feasibility Analysis, the potentiostat/galvanostat is the primary tool for electrochemistry. The potentiostat/galvanostat is usually one device, generally referred to as a potentiostat, which can either apply a potential or a current to an electrochemical cell. There are several techniques that potentiostat can perform. Cyclic voltammetry (CV) is a technique where the electrode potential is changed linearly with time while recording the current that is produced. With this method, one can observe electrochemical reactions occurring on the electrode. Figure 4 shows a single redox reaction indicative of the response that we expect to record using with this module. From voltammograms similar to that represented by the red trace, the reaction kinetics can be determined through data processing [19].
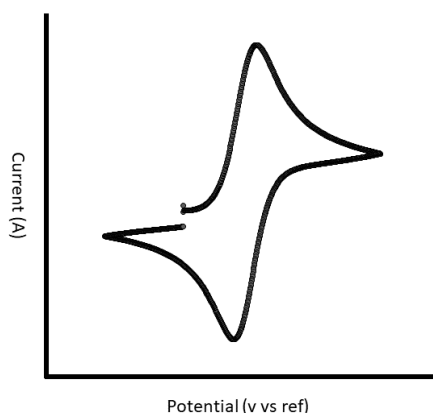
Figure 4. Example of a Single Electron Reaction CV

Another available technique is Chronoamperometry. In Chronoamperometry, a potential

step(s) is applied to the working electrode and the current response over time is recorded [20].

Depending on the process, the kinetics and/or the associated transport parameters for that process

can also be determined through data processing. For example, if the concentration of a dissolved

chemical species undergoing an electron transfer reaction is known, the diffusion coefficient of

that species can be determined from the experimental chronoamperometric data (Figure 5) using

the Cottrell equation [21].
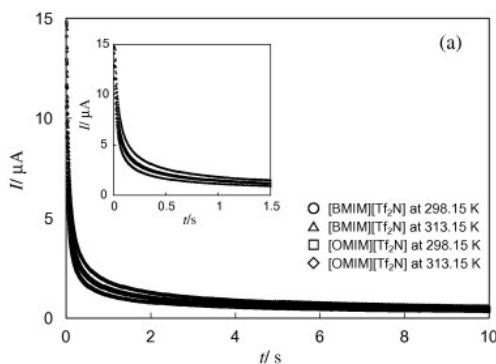
Figure 5. Chronoamperometric Curves of $[Fe(C_5H_5)_2]$ in $[BMIM][Tf_2N]$ and

$[OMIM][Tf_2N]$ at Atmospheric Pressure at 298.15 and 313.15 K on a Platinum Disk Electrode; I

vs. t [21]

Chronopotentiometry is another technique that can be performed by a potentiostat. In

Chronopotentiometry, a constant current is applied and the potential over time is recorded [20].

As with the other techniques, the respective kinetic information can be obtained from the

analysis of the data. The potentiostat has a variety of techniques at its disposal, mentioning all of

them is not necessary for this document as most electrochemical techniques rely on collecting

data for three universal variables, i.e., time, current and potential but under different

experimental conditions. Given that the cyclic voltammetry is the most used technique, it will be

the choice for the module. The analysis of CV data will be aided by electrochemical impedance

measurements.

b) *Computational module*

There are a variety of options that are available to do MD simulations. The three common

options are the Vienna Ab initio Simulation Package (VASP), Siesta, and NWChem. VASP is a

computer program used to do all-atom MD simulation using a plane-wave basis set as it

computes an approximate solution to the Schrödinger equation. Using different methods such as

density functional theory (DFT), solving the Kohn-Sham equations, or within Hartree-Fock (HF)

approach, etc. [22]. VASP is a computationally complex system and therefore is best to use with

small systems so that the time to complete the simulations is relatively short. However, when

compared to simulations of the same system, the VASP results have better accuracy than a

program such as Siesta [23]. NWChem, like VASP, is a computer program used to do all-atom

MD simulation. It has the same many of the same functions as VASP [24]. Like VASP, it too

sufferers from a massive time complexity [25]. Siesta is the last program that is a candidate to be

a part of the computational module. Like the programs listed before, it can do all the same

methods using a numerical atom-centered basis set [26]. In Siesta, the time complexity is linear

and scales well with extensive simulations [23]. In the selection of MD methods, intangibles,

such as familiarity with the method, are also considered.

The following set of criteria and their associated weights were used to evaluate the three

alternative techniques for the design and implementation of the computational module.

- The scalability criterion is the ability to handle different simulation sizes without

    drastically increasing computational time.

- The familiarity criterion is what software the operators and advisors are familiar

  with their work. Familiarity is essential as it affects the time spent implementing

  the module.

- The accuracy criterion is how accurate the data collected from the simulation will

  be.

Table 6 provides the comparison (weighted decision matrix) to evaluate the three

alternative techniques for the design and implementation of the computational module. The

selection was made based on a set of criteria and their associated weights. Based on the selection,

Siesta will be the preferred architecture.

Table 6. Decision Matrix for Computational Module

		VASP		SIESTA		NWChem	
Criteria	Weight	Rating (0-100)	Score W*R	Rating (0-100)	Score W*R	Rating (0-100)	Score W*R
Scalability	0.4	70	28	90	36	70	28
Familiarity	0.35	30	12	90	36	30	12
Accuracy	0.25	80	32	70	28	80	32
			72		100		72

c) Material Characterization module

In this module, there are no alternative methods. The customer has chosen to run X-ray

absorption and scattering measurements as the preferred method to determine the material's

structure. This module will occur at Argonne National Laboratory at the Advanced Photon

Source (APS), a user facility. With all the choices made the selected system architecture is

presented in Figure 6.
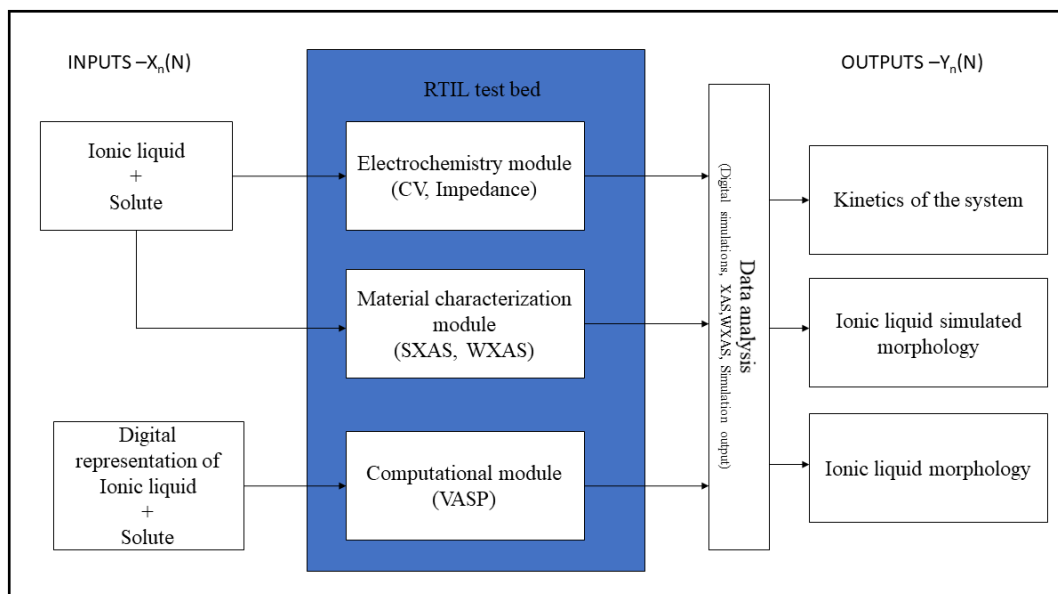
Figure 6. Selected System Architecture

The system is designed to take an ionic liquid with a solute as its inputs. The IL could be a

mixture of or a pure liquid. The solute will be chosen based on the selected redox reaction,

typically a single electron transfer reaction. There will be a digital representation made for MD

simulation purposes. For the electrochemical module there will be a battery of CV's performed

under various conditions. In the material characterization module samples will be made

comparable to the samples used in the electrochemical module and taken to APS. There XAS,

WXAS, and XANES techniques are used. After the analysis of all the data a report will be

made.

3. Architecture Requirement Allocation and Verification

This section discusses the allocation of the system requirement to the various elements of

the selected architecture and verifies that the selected architecture will meet all the system

requirements. The system requirements specifications, as seen in Table 7 were allocated for the

three modules of the SOI: electrochemistry module (EM), computational module (CM), and the

material characterization module (MM).

Table 7. System Requirements Specifications with Mapping to SOI Elements

System Requirements		SOI Element
1.1	A manual shall be created to document procedural needs of utilization of the subsystem	EM, CM
1.2	The manual shall facilitate directions for system operation and calibration techniques to anyone with standard lab training	EM
1.3	The system shall be physically adaptable to different test cells and Electroanalytical techniques	EM
1.4	The system shall be physically adaptable to different test cells and electrochemical analytical techniques	EM
1.5	The system shall output current-potential data under cyclic voltametric conditions data at numerous scan rates within the range between 1 and 5000 mV/s	EM
1.6	The system shall output radial distribution functions of the CU-Cl ion pair	CM
1.7	The system shall output 1D X-ray scattering patterns	MM
1.8	The system shall use Siesta to perform the molecular dynamics simulations	CM
1.9	The system will only be verified for criteria that fall within a 10% error of the expected value	EM, CM, MM

Chapter 3: Production Stage

The SE activities in this stage include the detailed design and development of the various elements comprising the SOI architecture. The production stage covers several steps, including the development of design requirements for lower-level system components, implementation of technical activities for fulfillment of design objectives, integration of system elements and activities, utilization of design tools and aids, preparation of design data and documentation, development of prototypes and models, implementation of design reviews and evaluations, and incorporation of design changes.

A. Implementation

This section discusses the design and development subsystem of the SOI. The elements are developed and integrated into an incremental process until the final system is achieved. The final system is then validated through testing, simulation, and others to meet the overall system requirements.

1. Ionic Liquid Sample Preparation

The Ionic liquid solution used in the electrochemical and material characterization module is either 1-Hexyl-3-methylimidazolium chloride (HMIM Cl), Figure7 A, with copper chloride ($CuCl_2$) or a mixture 1-Hexyl-3-methylimidazolium bis(trifluormethylsulfonyl)imide (HMIM Tf_2N), Figure 7B, HMIM Cl, and $CuCl_2$. The copper chloride could be hydrated or anhydrous, as seen in Figure 8. For this dissertation, the mixture is composed of 18 % by weight of HMIM Cl and 82 % by weight of HMIM Tf_2N. This solution is labeled the Mixture 2 for the rest of the text,

as seen in Figure 7. In either sample, the first step is to determine the water content of the

solution without $CuCl_2$ using a Karl Fisher titrator. Since copper salts interfere with the titration

process, the measurement has to be taken without $CuCl_2$. With the amount of water in the IL

known, one can prepare solutions containing different Cu (II) concentrations and Cu (II) to water

concentration ratios. for all samples and can be adjusted for any solute and IL.

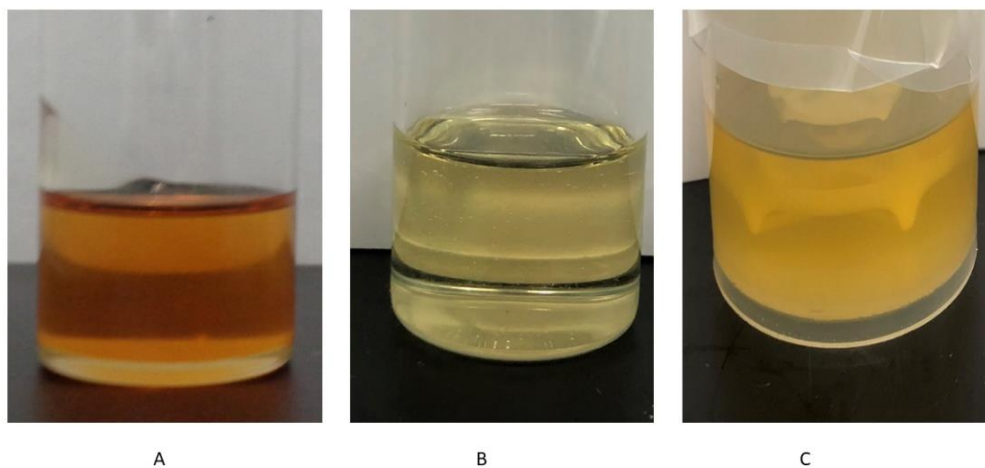A   B   C

Figure 7. A) 1-Hexyl-3-methylimidazolium Chloride, B) 1-Hexyl-3-methylimidazolium Bis(trifluormethylsulfonyl)imide, C) Mixture of 1-Hexyl-3-methylimidazolium Chloride and 1-Hexyl-3-methylimidazolium Bis(trifluormethylsulfonyl)imide
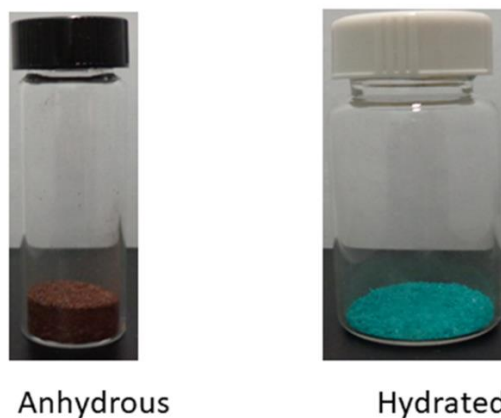

Anhydrous   Hydrated

Figure 8. Copper Chloride Powder Used in Making IL Solution

The chosen copper (II) chloride concentrations are 25, 50, and 100 mmol dm^{-3}. Both

hydrated and anhydrous copper chloride are used in these experiments. For each CuCl$_2$

concentration, several solutions with different water to Cu (II) concentration ratios were made.

For the solutions in HMIM Cl, the ratios used were 20 to 1, 40 to 1, and 80 to 1. For mixture 2,

low water to copper molar ratio (7 to 1, 4 to 1, and 2 to 1, depending on the copper

concentration), 20 to 1, 40 to 1, and 80 to 1 ratio were used. For each solution, the base IL is

weighed in a glass vial. Using the weight of the base IL the amount of copper needed to create a

solution with the desired concentration is calculated using Equation 1, where m$_x$ is the mass of

the solute (CuCl$_2$ or CuCl$_2$.2H$_2$O), M$_X$ is its molar mass, and V$_{sample}$ is the volume of the liquid,

which was calculated from the weight of the base IL and its density.

$$C_X = \frac{m_x}{M_x * V_{sample}} \qquad (1)$$

Next, the amount of water in the sample after adding the copper chloride is calculated.

Using equation 1 and the water concentration from Karl Fisher titration, one can calculate the

mass of water in the sample before copper chloride addition. Next, the amount of water

introduced with copper chloride (two or zero moles of water for each mole of hydrated or

anhydrous CuCl$_2$ respectively) is added to the initial water amount as determined by Karl Fisher

titration. The calculation will give a new concentration of water. Now that C_{H_2O} and C_{CuCl_2} were

determined, one can calculate the C_{H_2O}/C_{CuCl_2} ratio and how close it is to the desired ratio.

From the known sample volume and the C_{H_2O}/C_{CuCl_2} ratio, one can calculate how much water

has to be added to achieve the desired C_{H_2O}/C_{CuCl_2} ratio. Using the calculated value, deionized

water is added with a single-channel pipette to an accurate value that the pipette can offer. Then

one can recalculate C_{H_2O}, C_{CuCl_2}, and C_{H_2O}/C_{CuCl_2} for data processing purposes. While this can

be done by hand, it is easier with multiple samples to use a spreadsheet program like excel. This was done

2. Electrochemical Module

a) Electrode Components.

Depending on the planned measurements, an electrochemical cell can be equipped with two, three, or more electrodes. For these experiments a three-electrode configuration consisting of working, counter, and reference electrodes was chosen. The setup allows for the simultaneous measurement of the working electrode current and potential. A glassy carbon electrode with a geometric surface area of 0.00785 cm^2 was selected for the working electrode, as seen in Figure 9.
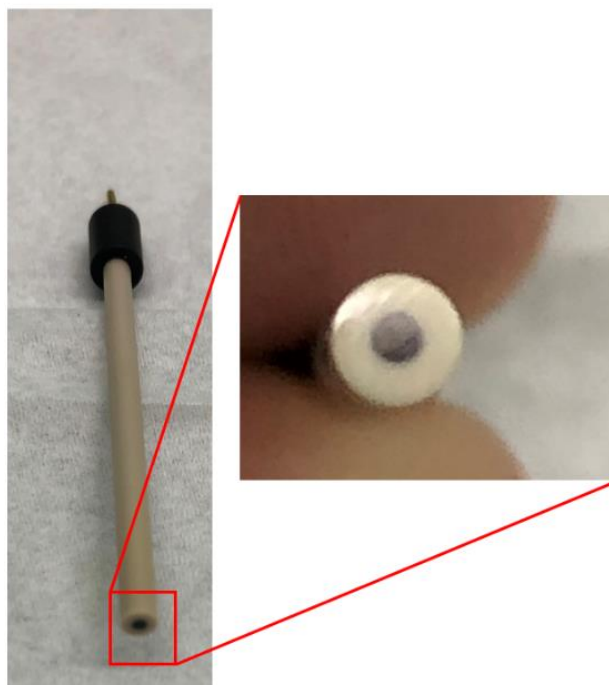
Figure 9. Glassy Carbon Working Electrode

Glassy carbon electrodes are not as catalytically active as Pt, leading to lower background currents. A platinum mesh was chosen as the counter electrode, as seen in Figure 10. Compared to the working electrode, a large counter electrode surface area ensures that the counter electrode is not significantly polarized during measurements and the voltage between the working and the counter electrode does not exceed the maximum voltage the potentiostat can deliver. In order to provide a stable reference potential against which the working electrode potential is measured, a real reference electrode was fabricated utilizing an electrochemical equilibrium between Ag (I) and Ag metal. As opposed to quasi-reference electrodes frequently used for experiments in ionic liquids, the potential of a real reference electrode is not affected by the studied solution composition.

Figure 10. Platinum Mesh Counter Electrode Inside Teflon Cap

The components of the reference electrode, Figure 11, are as follows: glass tube, glass frit, shrinkable Teflon sleeve, silver wire. The assembled reference electrode is shown in Figure 12. The glass frit attached to the bottom of the tube with the Teflon sleeve prevents mixing the studied solution and the internal reference electrode solution. The latter was prepared (0.01 mol dm^{-3} AgCl in HMIM Cl) by diluting a 0.1 mol dm^{-3} AgCl solution in HMIM Cl with pure HMIM Cl.   In order to ensure the necessary electrical (ionic) contact between the internal solution of the reference electrode and the studied solutions, the former had to permeate through the glass frit. Due to the high viscosity of some ionic liquids, the time required for the full frit permeation is rather long, approximately 3 days. Therefore, preparation of the reference electrode may need to take place well before the preparation of the IL sample based on the user's time frame.
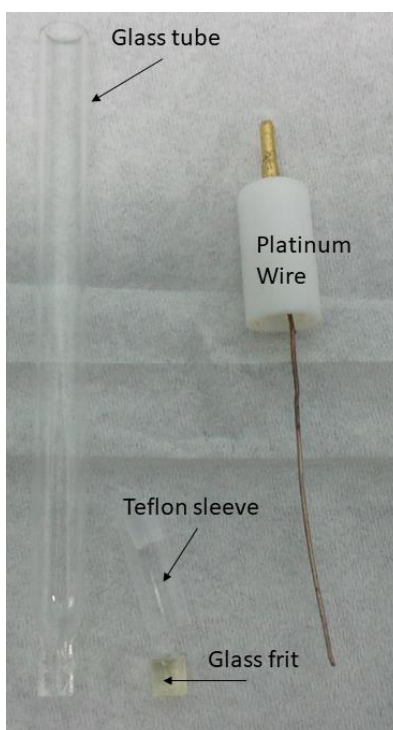
Figure 11. Reference Electrode Components

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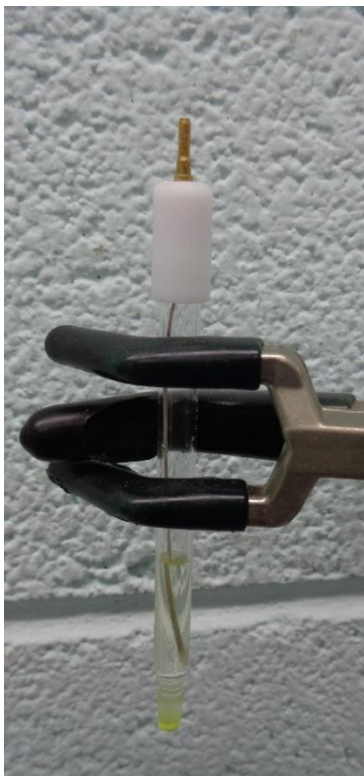
Figure 12. Completed Reference Electrode

b) Electrochemical Cell Preparation.

With all the components assembled and prepared, the electrochemical cell must be put together. In these experiments, a concave vial was used, Figure 13, so that one would only need small quantities of the IL for the experiments.

Figure 13. Conical Vial

     Once the vial is cleaned with isopropanol and dried, the IL solution is poured into the

clean vial. One can insert the electrodes into a Teflon cap seen in Figure 10. The cap is then

inserted into the top of the vial. Short wires equipped with alligator clips are attached to the leads

of the electrodes and subsequently wrapped the vial in aluminum foil to prevent a photochemical

effect, discussed later. The cell is placed into a plastic bag and the wires are pulled through an

opening left to accommodate them. Then, excess air is removed from the bag and the bag is

sealed it to reduce air exposure. Finally, the wires are connected to the potentiostat/galvanostat

leads to start the electrochemical tests (Figure 14).
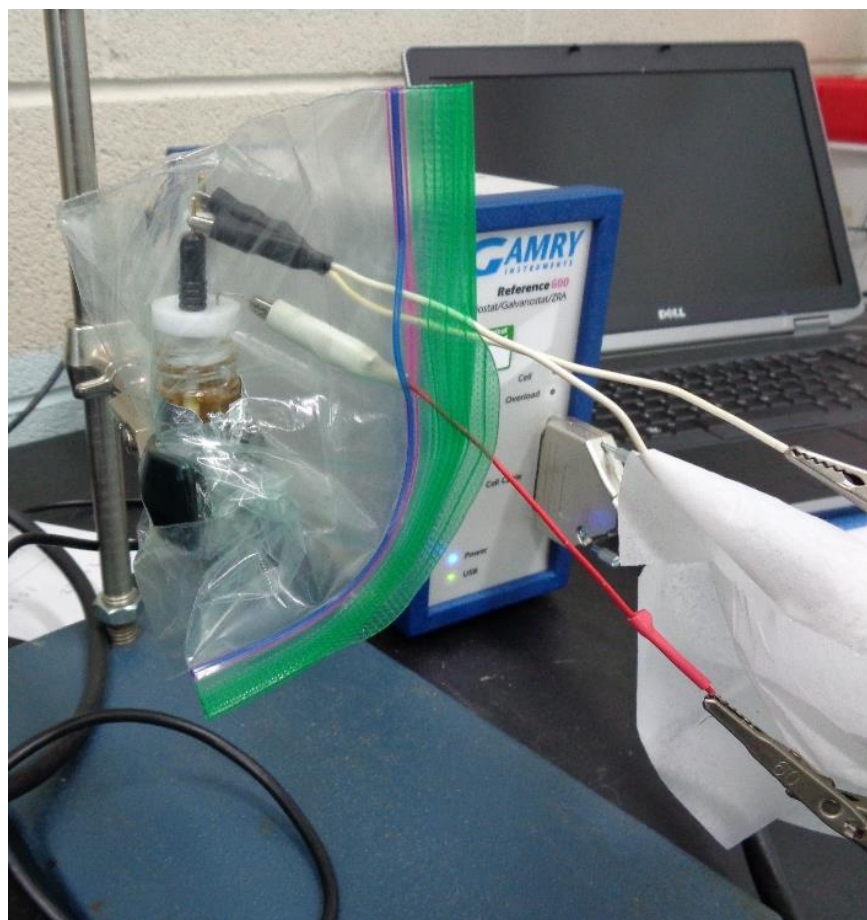
Figure 14 Completed Electrochemical Cell

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c) Cyclic Voltammetry.

Cyclic voltammetry (CV) is an electrochemical technique employed to investigate the chosen solute's reduction and oxidation processes. The basic concept behind a CV is that a potentiostat/galvanostat applies a cyclic voltage between the working and reference electrode while recording the current between the working and counter electrode. The voltage moves through the desired potential range at a set voltage change per second, called a scan rate. Several operating parameters must be inputted into the potentiostat/galvanostat control software, e.g., the scan rate, the initial and the reversal potentials, etc., to run a CV. This step requires some knowledge of the electrochemical properties of the studied solution to correctly select the operating parameters. If there is no prior knowledge of the system, the user must do some preliminary experiments to find the operating parameters. The next step is to determine the so-called potential window, i.e., the voltage range where the IL will not electrochemically break down due to the applied voltages. In order to determine the potential window, one must perform the voltammetry without the solute in the sample, as seen in Figure 15.
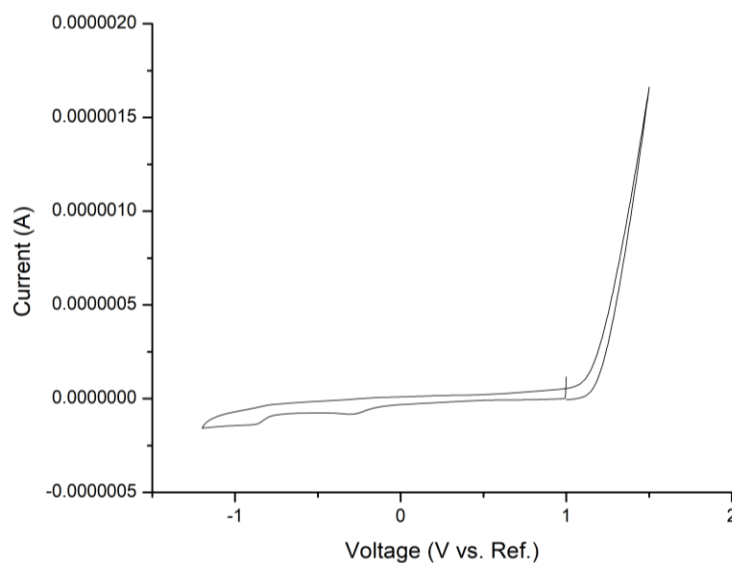
Figure 15. Potential Window of Pure HMIM Cl

Then a sample containing a solute is made and a voltammogram is recorded for the same

potential range, noting where the reaction of interest occurs, as seen in Figure 16. Then, the

optimal voltage range, where no electrochemical reaction except the studied one occurs, is

selected. This will be the scan range. In these experiments, that range is from 0 V to 1 V. The

initial potential of the CV was selected to be 1 V. At this potential, the only stable oxidation

state of copper is +2. The whole scan will start at 1 V, go to 0 V then back to 1 V for one scan.

The scan rates chosen are 20, 50,100, 200, 500, and 750 mV/s with a second 20 mV/s scan after

running the previous CVs. Other parameters in the software setup are not crucial to these

samples and vary depending on the software used; the electrochemist will have to set those

parameters if need be.
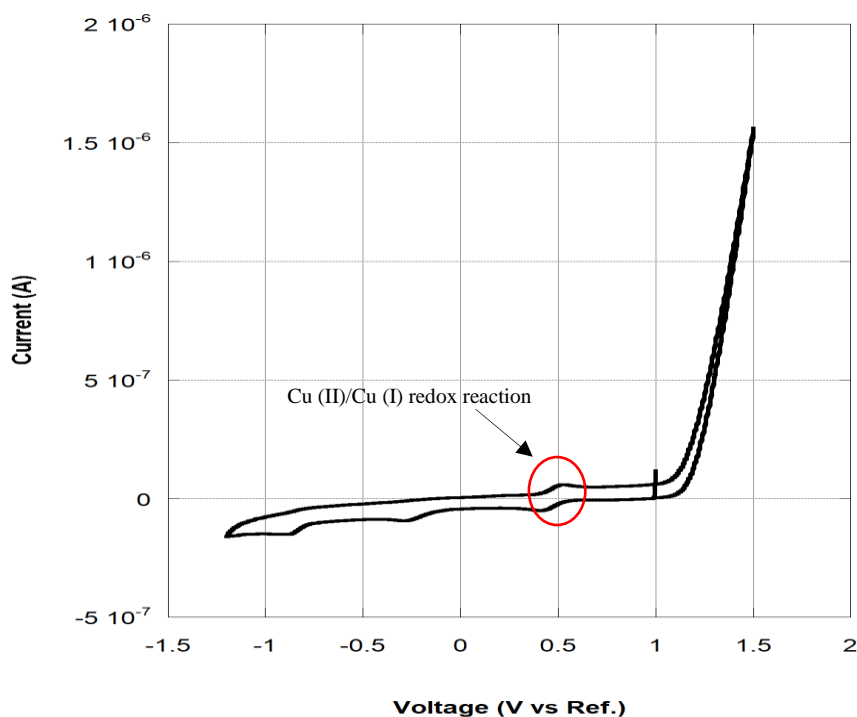
Figure 16. Potential Window of Pure HMIM Cl with CuCl$_2$

e) Electrochemical Impedance Spectroscopy.

Impedance Spectroscopy is a way to measure complex electrical resistance. Electrical resistance is the ability of a circuit element to resist the flow of electrical current. Most commonly, Ohm's law governs the electrical resistance. However, most circuits typically have capacitors and inductors that exhibit much more complex behavior than a simple resistive system. Impedance spectroscopy works by using a potentiostat/galvanostat to apply a sinusoidal voltage to an electrochemical cell. This voltage produces an alternate current whose amplitude and phase depend on the applied voltage frequency and the electrical properties of the system. A Nyquist plot is the plot of the imaginary (phase shifted) part of the impedance against its real part and is the preferred representation of the recorded impedance. The complex impedance can give electrochemical information about the system. Typically, to get that information, after the experiment is ran, one must fit the data to an equivalent circuit. The fit is based on general knowledge of the system, using a program that models equivalent circuits using impedance data. The modeled circuit elements can be either ideal (e.g., resistors or capacitors) or not ideal (e.g., constant phase elements). However, due to the complexity of the equivalent circuit for these solution/solute pairs, a choice was made to use the impedance spectra to estimate the internal resistance. The internal resistance is needed for data processing the CV data.

f) Mitigating Photochemical Effect.

During preliminary experiments, a photochemical effect, which lead to the bulk reduction of Cu (II) to Cu (I), was discovered. This effect is undesirable in the data processing aspect as it makes it impossible to know the initial Cu (II) concentration, a physical parameter used in the process. To mitigate this effect, the working electrode is held at 1 V for a long time to ensure that copper in the area around the electrode is exclusively in +2 oxidation state (Cu (II)). Applying

similar procedures may not be required for other IL/solute mixtures whose electronic properties

are different. While there are different ways to oxidize any Cu (I) present in the electrode

vicinity to Cu (II), the chronoamperometry technique was selected to perform this task. The

electrode was held at an open circuit potential for 0.5 seconds and then at 1 V for 10 minutes.

After that, a CV was recorded. As the initial potential of the CV (1 V) was equal to that applied

during the preceding chronoamperometry, there was no sudden change of the solution

composition at the solution/electrode interface and no associated current spike at the initial

potential, which could affect the subsequent data analysis.

g) *Mitigating Effects from Cyclic Voltammetry.*

During preliminary experiments, it was found that every CV recorded had an effect on

the subsequent CV. The effect was due to the non-uniform concentrations of the electroactive

species (Cu (II) and Cu (I)) in the electrode vicinity resulting from their slow diffusion and the

perturbation caused by the voltammetry. To mitigate this effect, a delay of 1 hour was initiated

between subsequent voltammograms. It is essential to note that the required delay may be longer

or shorter for other ionic liquids, depending on their viscosity

h) *Module Experimental Procedure.*

The software controlling the potentiostat/galvanostat allows the use of scripts to run

experiments without manually starting each electrochemical technique. This allows for an

accurate and repeatable experimental procedure for each sample made. In the present

experiments, script was as follows: Chronoampometry for 10 minutes at 1 V, 20 mV/s CV, delay

for 1h, Chronoampometry for 10 minutes at 1 V, 50 mV/s CV, delay for 1h, Chronoampometry

for 10 minutes at 1 V, 100 mV/s CV, delay for 1h, Chronoampometry for 10 minutes at 1 V, 200

mV/s CV, delay for 1h, Chronoampometry for 10 minutes at 1 V, 500mV/s CV, delay for 1h,

Chronoampometry for 10 minutes at 1 V, 750 mV/s CV, delay for 1h, Chronoampometry for 10 minutes at 1 V, 20 mV/s CV, delay for 1 h, Impedance spectroscopy. This script can also be modified to run experiments over several days to perform time-resolved studies. All experiments were performed at room temperature, 25 ⁰C.

i) Data Processing for Electrochemical Module

After each series of experiments, the CV data were processed using the DigiElch 8 software from ElchSoft. This software allows the user to create simulations/fittings of the experimental data to extract the relevant kinetic and thermodynamic properties. To simulate/fit the data, the program needs experimental parameters such as internal resistance, species concentration, electrode surface area, and temperature. The following Figure 17 shows the interface the user will have to familiarize themselves with.
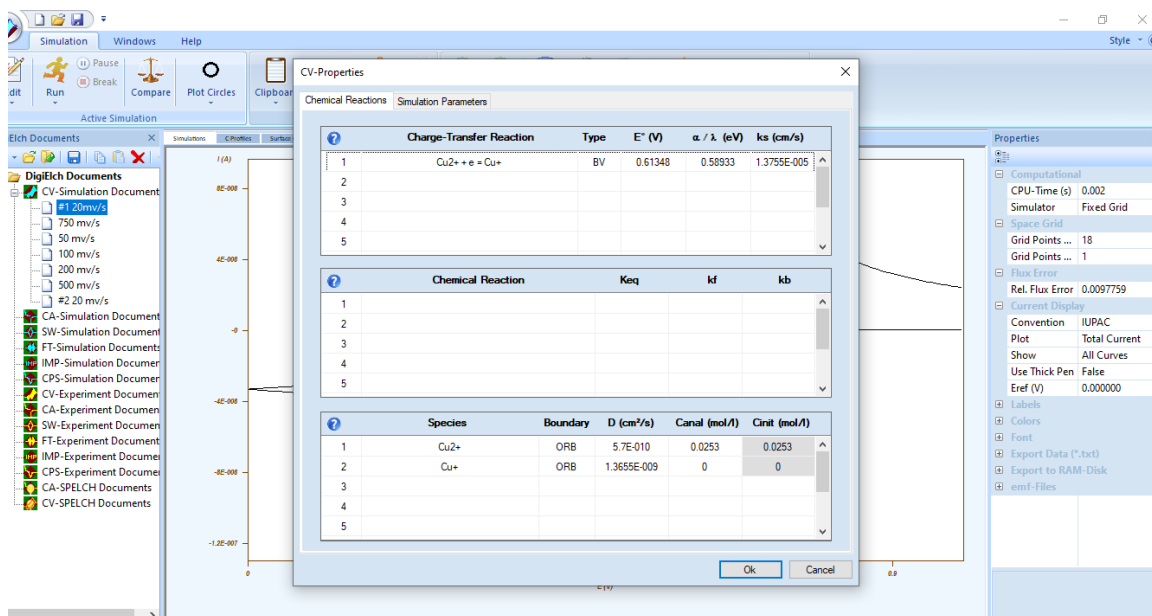

Figure 17. DigiElch 8 Software Interface

3. Material Characterization Module

a) Using the X-ray Facility.

This module requires the use of the Advanced Photon Source (APS) located at Argonne National Laboratory. APS provides ultra-bright, high-energy storage ring-generated x-ray beams for research in almost all scientific disciplines. APS is a user facility where it is free to use as long as the experiments performed are not proprietary. In order to be granted a beam time, one has to first register with the APS User Office to receive a badge number and begin the site access approval process. One can visit the APS website to start the process, https://beam.aps.anl.gov/pls/apsweb/ufr_main_pkg.usr_start_page. Once the registration is issued, one can submit a proposal. The one used in this dissertation is the General User Program, which allows researchers from anywhere in the world to use the APS facility through a competitive access process. The proposal describes the experiment(s) and identifies the experimental team. For these experiments small-angle x-ray scattering (SAXS) and wide-angle x-ray scattering (WAXS) were chosen. If the user does not exist in the APS system, they will need to establish a legal agreement between APS and the user's home institution. Also, the user would need to make a user account, if one is required, by setting up a purchase order to pay for supplies and services or proprietary beam time. After a beam time is awarded, the user will need to complete all training required by APS (if the user is visiting the facility). If the user needs the samples delivered, they will need to arrange for delivery. If APS requires, the user will also need to arrange for disposal/return of samples/materials. After the user has completed the experiment, they will need to complete an End of Experiment form; the experiment spokesperson receives instructions if APS is disposing of the samples. Finally, the user must acknowledge the APS and

the beamline in any resulting publications, notifying APS of publications resulting from APS

data.

b) *Sample Preparation.*

To prepare ionic liquids and ionic liquid solutions for characterization, APS requires

them to be placed into capillaries, glass, or quartz. Pasteur pipet tips (glass) were chosen as the

capillaries for these samples since the glass capillaries that were ordered were brittle and often

broke. To prepare the capillaries the tips of the Pasteur pipets need to be separated from the

body through glass cutting. Once separated, the smaller portion of the Pasteur pipet can be flame

sealed on one end with a blowtorch. Through the use of a syringe one can place the various IL

solutions into the separate tips. A centrifuge was used to drive the IL solution into the bottom of

the sealed tip. If that particular sample needed more solution in the capillarity, the process was

repeated. Once filled, the other end of the tip was sealed. When all the samples were ready, they

were placed in the sample holders provided by APS, noting the position of each sample. That

information was submitted to APS through an online portal. Then the samples were packed

carefully and mailed to APS.

c) *Data Processing for Characterization Module.*

The X-ray scattering data comes in the form of 2D images, as seen in Figure 18. The user

will then check the 2D image for essential features, such as anisotropic patterns. If circularly

isotropic, the X-ray scattering domains are randomly oriented. If the 2D image shows circularly

anisotropic patterns, the user can extract the orientation distribution of ordered domains present

in the sample. Then the user can convert the 2D image to a 1D image. This is typically a plot of

intensity (log scale) vs. scattering vector q (linear scale). The magnitude of the vector q is

defined as $4\pi\sin\theta/\lambda$, where theta is half of the scattering angle and lambda is the X-ray

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wavelength [27]. The 1D image is subsequently examined to determine if Bragg peaks or just

smeared features are present (Figure 18). Depending on the image features an applicable data

analysis is applied.
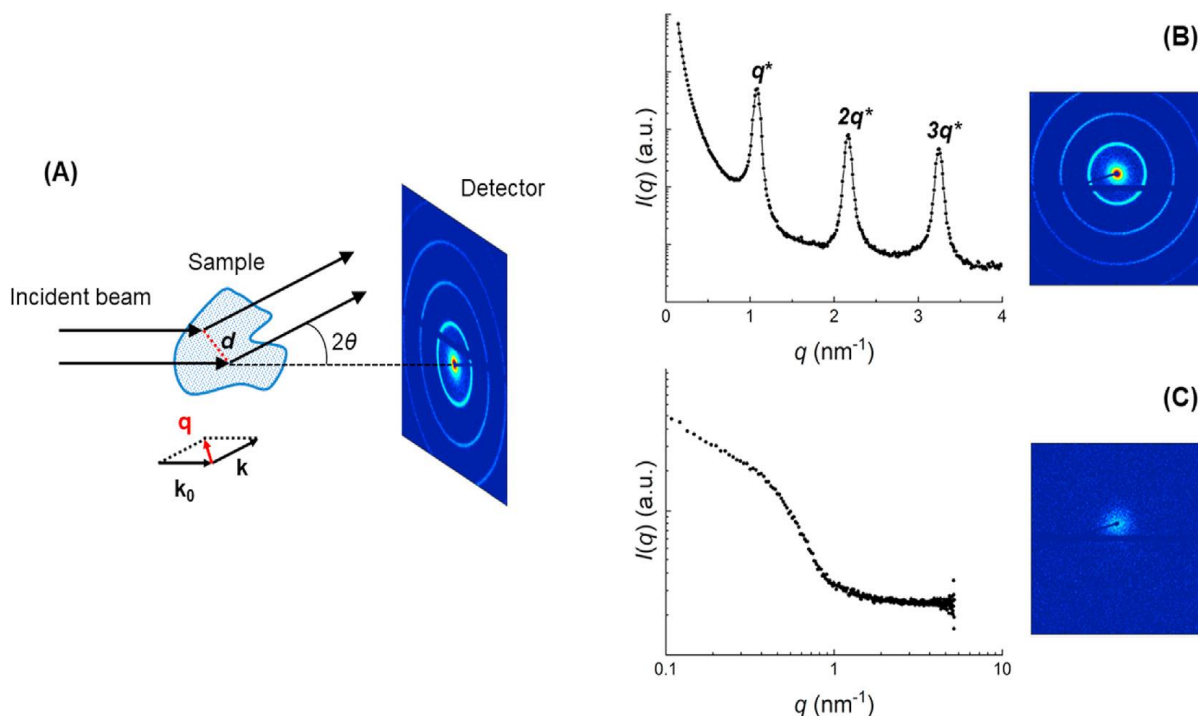
Figure 18. Example of 2D SAXS Image [27]

4. Computational module

a) Model Components.

To begin the user must digitally create or get components of IL and the solute. There are

several ways to do so. The easiest way is to use a free material database to obtain a file that

contains the structure of the molecules that one intends to study. In this project, when the files

were available, a protein database file (pdb) was used from https://www.rcsb.org/. The pdb file

contains the starting coordinates of the select molecule or protein. If the files were not available

it may be possible to get an input file from PubChem, https://pubchem.ncbi.nlm.nih.gov/. If this

method is used, one has to convert the respective file to the pdb format. If neither of these

methods work, one can create their own input file using a program like Avogadro. Avogadro is

an advanced molecule editor and visualizer. The structures of ions of the ionic liquids used in

this study and obtained using Avogadro are shown in Figure 19. It is important to note that the

input file using all above methods can be created in a Windows environment.
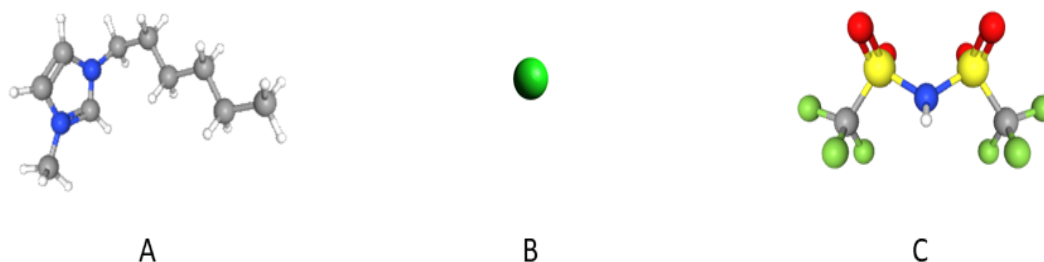
Figure 19. Ball and Stick Digital Representations of A) 1-Hexyl-3-methylimidazolium B)
Chloride Ion C) Bis(trifluormethylsulfonyl)imide

b) *Creating a Digital Sample.*

Once the input files are prepared, they can be transferred to the computational Linux

environment and used to create a digital sample. In order to create a digital sample, the input

components are placed virtually in a 3D cell and multiplied using a program called, Packmol. In

Packmol, the user defines the 3D space and fill it with the selected number of molecules. The

program approximates the positions of the molecules. The input parameter for Packmol are as

follows: tolerance, file type of the input file(s), output file name, structure input. The tolerance

parameter is the minimum distance, in angstroms, between pairs of atoms of different molecules

for systems at room temperature and pressure. The structure input has three parameters: input

file, number of molecules to be mixed, and the cell size in angstroms. Each molecule added to

the cell needs its own structure file, Figure 20. The output of Packmol is a defined volume with

the number of molecules the user specified, Figure 21.

Figure 20. Packmol Instructional Code for HMIM Cl

Figure 21. Visual Representation on how Packmol Works
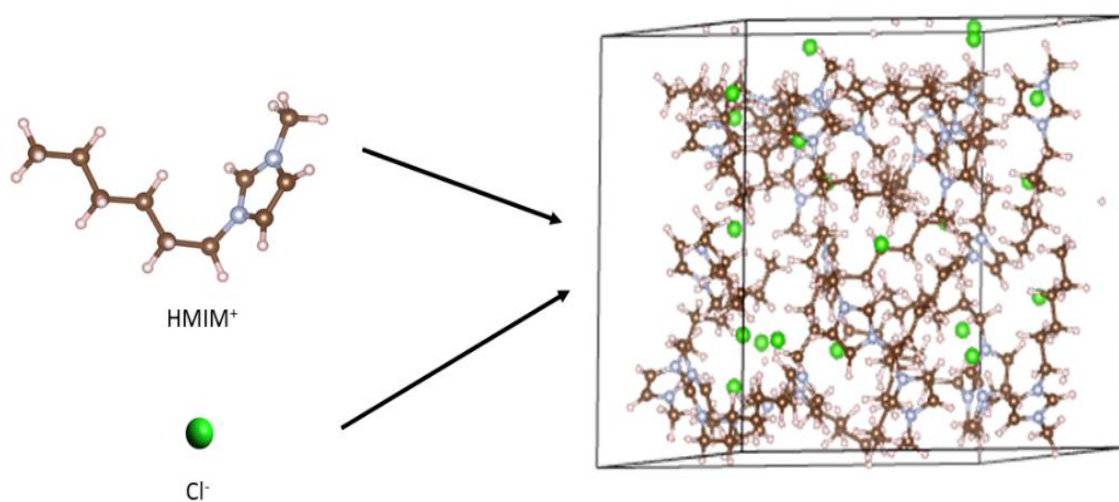
c) *Creating the Siesta Input File.*

Once the Packmol pdb output file is created, it has to be converted to a file that is usable in SIESTA, defined in the Alternative Architecture Definitions and Architecture Selection. This process has several steps depending on the operating environment of the system. In the operating environment of Linux, the first step is to convert the pdb file to a gin file type. This was done by copying the important information from the pdb to a gin file by adding information to the head and the tail of the file. The gin file is the input file of the General Utility Lattice Program, and the output file is a gulp (General Utility Lattice Program) file. The focus of the GULP code is on analytical solutions of boundary conditions, using lattice dynamics. The gulp file was converted to an fdf file with added information in the header. Once the fdf file was ready, it could be used in SIESTA program.

d) *Initial Relaxation.*

Now that the user has a digital sample to work with the process of preparing that sample begins. The sample is put through a process called relaxation. This process does a series of calculations to find the optimal positioning of all the molecules. The simulation achieves relaxation when the stress, an output parameter, of the system has reached a minimum. The header, or top of the input file, mentioned in the last section contains the input parameters. To start the relaxation, process the user has to input the correct parameters into the header of the FDF file. The input parameters in Figure 22 are for the relaxation process. When the relaxation process is finished, SIESTA creates a new fdf file as the output file.

```
SystemName                hmimclnoH2O
SystemLabel               hmimclnoH2O

MaxSCFIterations          200
DM.MixingWeight           0.3
DM.NumberPulay            3
DM.Tolerance              1.d-3
DM.UseSaveDM

PAO.BasisSize             SZP
PAO.EnergyShift           300 meV
MeshCutoff                150.0 Ry

SolutionMethod            diagon
ElectronicTemperature 300 K
Harris.Functional         .true.
MD.TypeOfRun              CG
MD.NumCGsteps             500|
MD.MaxCGDispl             .2 Ang
MD.MaxForceTol            0.04 ev/Ang

TimerReportThreshold  1
```

Figure 22. Input Factors Used for Relaxation of Sample

e) *MD Simulation Data.*

Once the system has relaxed, one can perform the Molecular Dynamics simulations. This

requires a change in input parameters, Figure 23. This is the data that that can be used to

calculate properties such as the radial density functions to understand the coordination spheres of

the copper in the system.

```
SystemName              hmimclnoH2O
SystemLabel             hmimclnoH2O

MaxSCFIterations        200
DM.MixingWeight         0.3
DM.NumberPulay          3
DM.Tolerance            1.d-3
DM.UseSaveDM

PAO.BasisSize           SZP
PAO.EnergyShift         300 meV
MeshCutoff              150.0 Ry

SolutionMethod          diagon
ElectronicTemperature 300 K
Harris.Functional       .true.

MD.TypeOfRun            NoseParrinelloRahman
MD.TargetStress         1.0Gpa
MD.InitialTemperature 300 K
MD.TargetTemperature   300 K
MD.FinalTimeStep        5000
MD.LenghtTimeStep        2.0 fs
MD.VariableCell         .true.
MD.UseSaveXV            .true.


TimerReportThreshold   1
```

Figure 23. Molecular Dynamic Simulation Input Parameters

B. System Verification

1. Electrochemical Module

a) *HMIM Cl Data.*

Using an electrochemical software, DigiElch 8, one can simulate the data to get the

kinetic parameters of the Cu (II)/Cu (I) system in HMIM Cl. Figure 24 shows a single scan rate

cyclic voltammogram and its digital simulation. The simulation slightly deviates from the

experimental data. That deviation remains within acceptable errors. For any scan rate, there are

six simulation parameters: standard potential, charge transfer coefficient, rate constant, diffusion

coefficient for Cu (II), diffusion coefficient for Cu (II). As the diffusion coefficient of Cu (I) is

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not experimentally accessible from the voltammetry of Cu (II), it was assumed that its value is

equal to that of Cu (II). Consequently, the standard potential determined by the simulation is

equal to the so-called reversible half wave potential. For every sample several scan rates, (20, 50,

100 etc.) were used. Typically, the simulation parameters for all scan rates should be the same.

The data in Table 8 demonstrate that the fitted parameters are identical at all scan rates within the

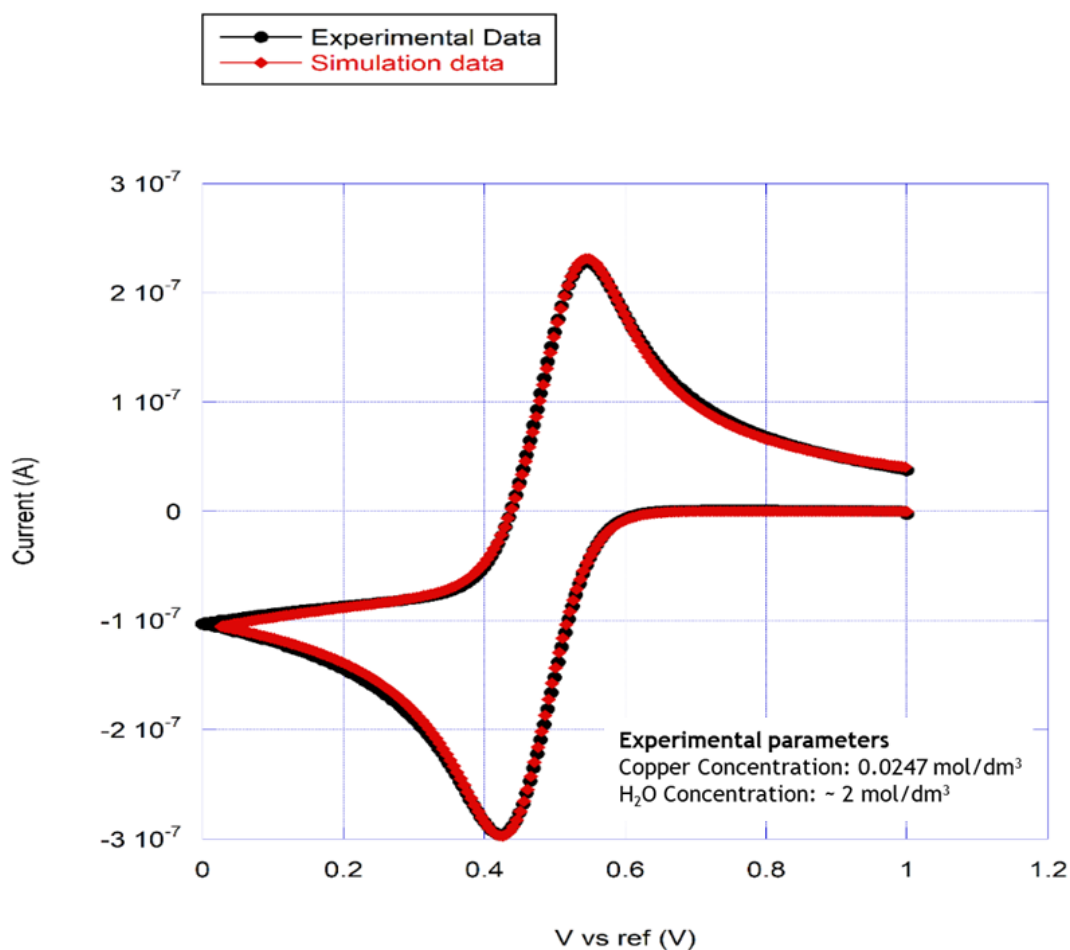limits of experimental error. Therefor the average of the values are reported.

Figure 24. Experimental and Simulated Data of CuCl2 in HMIM Cl

Table 8. All Simulations Parameters for HMIM Cl with 0.0247 mol/dm^3 of CuCl$_2$ with 1.9731 mol/dm^3 of water

Scan Rate	Ir	E*	α	k$_s$	Cu(II)	Cu(I)
mv/s	Ω	v		cm/s	cm^2/s	cm^2/s
20	7889	0.48844	0.47146	3.59E-05	2.13E-09	2.13E-09
50	7889	0.48628	0.46539	3.10E-05	1.90E-09	1.90E-09
100	7889	0.4868	0.47137	2.86E-05	1.90E-09	1.90E-09
200	7889	0.48766	0.45641	2.67E-05	1.90E-09	1.90E-09
500	7889	0.4904	0.44351	2.10E-05	1.75E-09	1.75E-09
750	7889	0.49513	0.39434	2.00E-05	1.75E-09	1.75E-09
20	7889	0.48795	0.47956	2.84E-05	2.13E-09	2.13E-09
Avg		4.89E-01	4.50E-01	2.72E-05	1.89E-09	1.89E-09
std dv		2.99E-03	2.69E-02	5.51E-06	1.27E-10	1.27E-10

By combing all the data for each sample one is able to see trends in the data. One can look at the data in terms of simulation parameter vs water content. For instance, Figure 25 shows a dependence of the kinetics on the water concentration.

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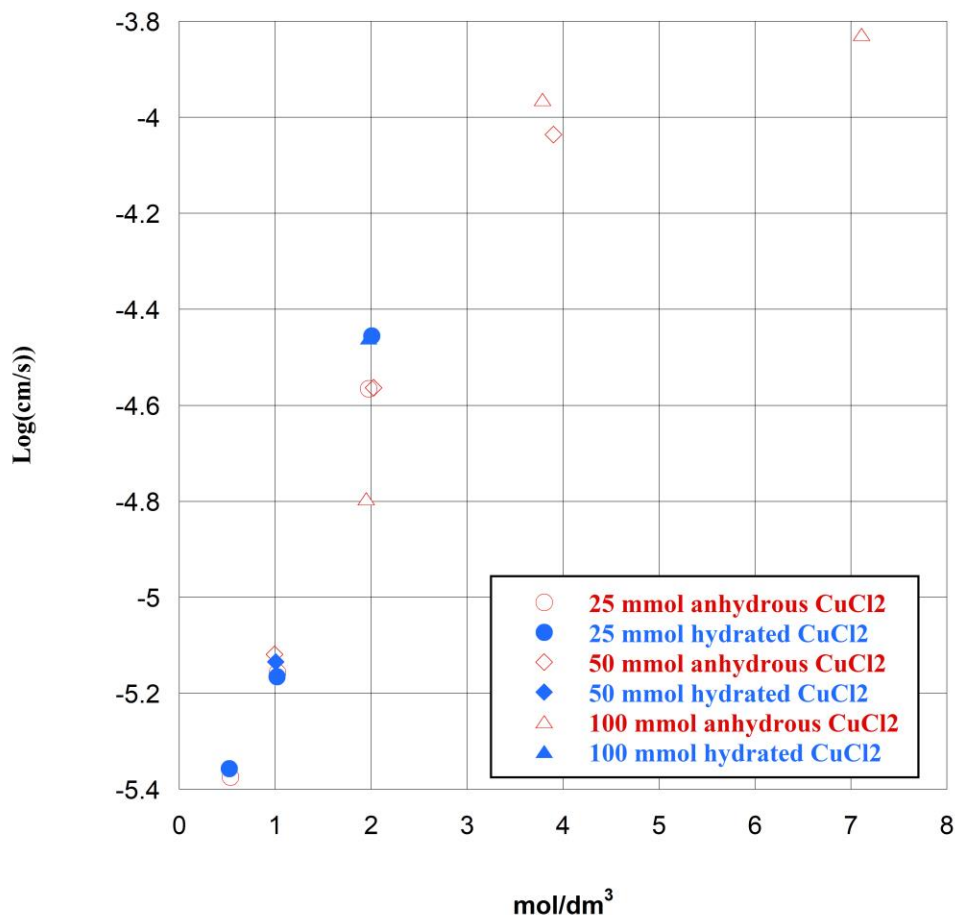**Figure 25**. Average k_s vs Water Concentration for HMIM Cl

The diffusion coefficients, Figure 26, showed a similar trend as the rate constant.

However, the diffusion coefficient values are more scattered. This is due to the high viscosity of

HMIM Cl, which makes the preparation of homogenous samples difficult. Similarly, using small

quantities of IL and solute may have contributed to the measurement errors.
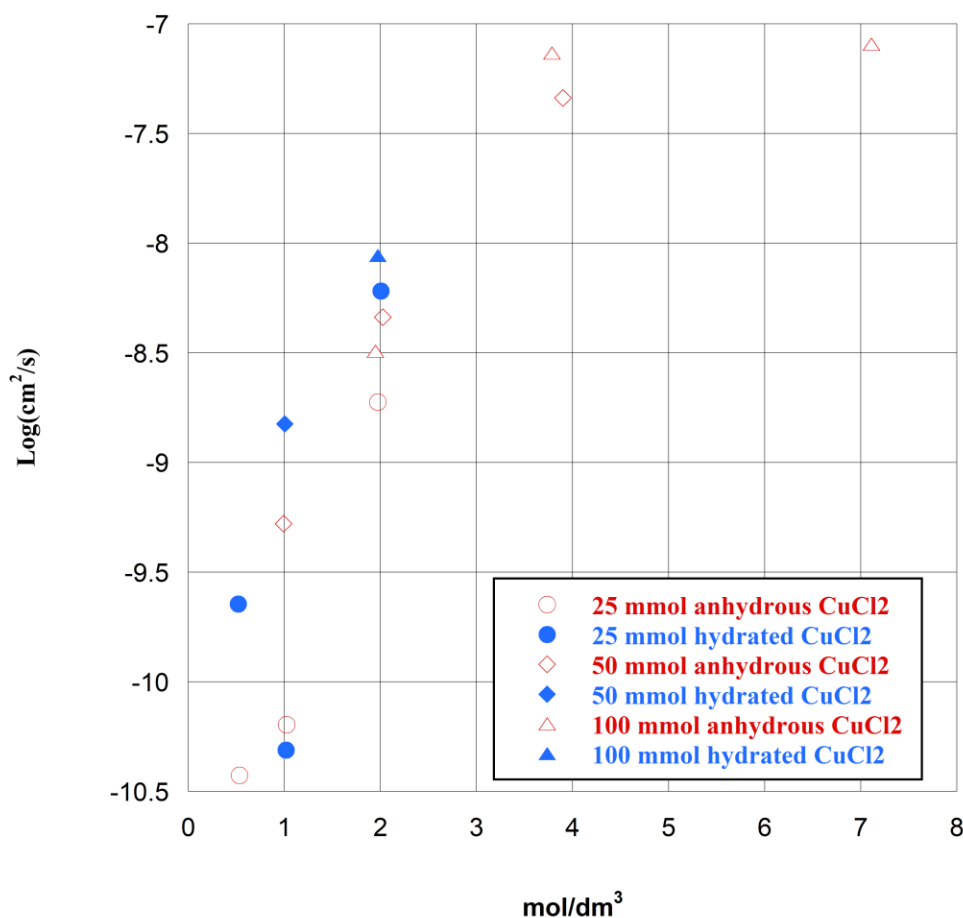
Figure 26. Average Diffusion Coefficient vs Water Concentration for HMIM Cl

The next parameter, the transfer coefficient doesn't appear to depend on water content within the water concentration range studied. There is just a scatter of data, Figure 27. The absolute value, which is below 0.5 suggests that the structure of the transition state of the reaction is slightly more similar to that of the substrate (Cu (II)) than of the product (Cu (I)). However, one cannot draw a definite conclusion about the effect of water concentration on the structure of the transition state in this case.
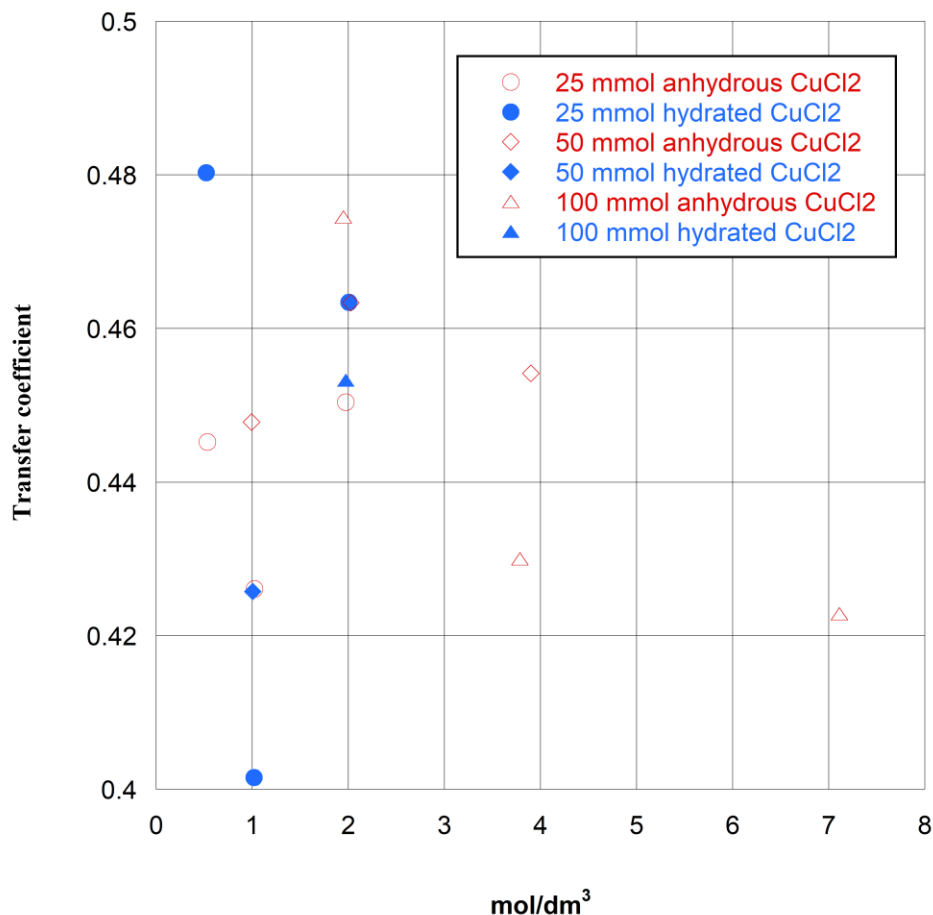
Figure 27. Transfer Coefficient vs Water Concentration for HMIM Cl

For the dependence of the reversible half wave potential on water concentration in HMIM Cl,

there seem to exist two trends, Figure 28. At lower water contents (≤ 2.0 M), a positive $E_{\frac{1}{2}}$ shift

with water concentration is observed, whereas the opposite is true for water concentrations

higher than 2 M. There may be two possible effects of water. The first is a change in the liquid

junction potential between the reference electrode and the bulk solution. There is always a

potential difference, the liquid junction potential, at the interface of two different electrolytes. In

this case the differences in the water concentration in the electrolytes contained in the reference

electrode and the electrochemical cell are the potential source of the liquid junction potential.

The second effect of water might be changes in the complexation of Cu ions by Cl⁻ with water

content. The magnitude and direction of the first effect is not easy to predict. The second effect is

expected to lead to a negative potential shift with the increasing water concentration (activity).

From this perspective, a decrease of the half wave potential with H_2O concentration at higher

water contents can be attributed to such a phenomenon, i.e., to the changes in Cu (II) and Cu (I)

complexation by chloride with increasing water content. Consequently, the predominant effect of

water on the half wave potential at low water contents most likely results at least in part from

changes of the liquid junction potential. If both diffusion coefficients change in a very similar

way with water concentration, the dependence of E_0 vs water content will be very similar to
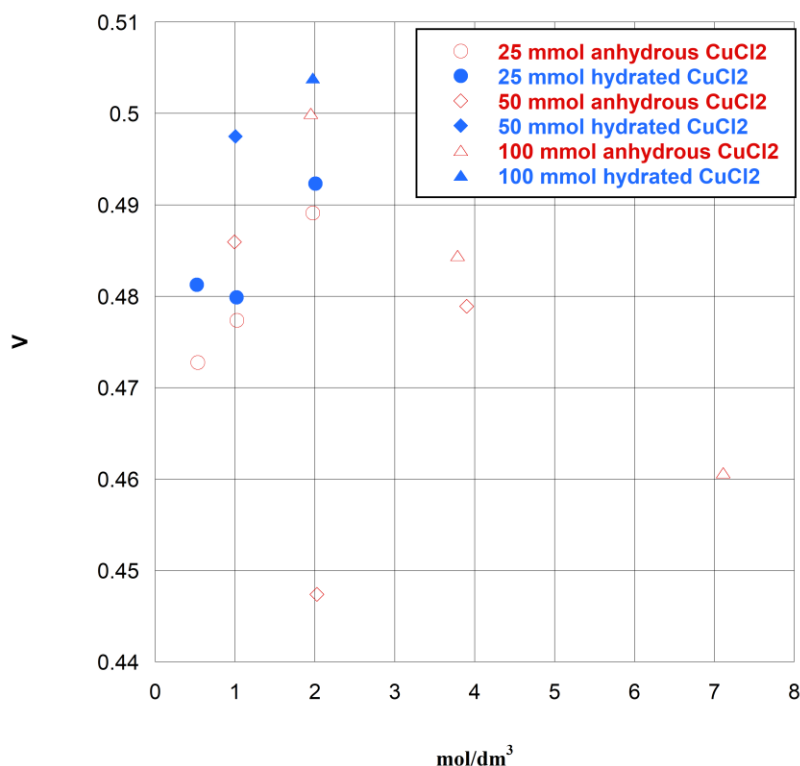
$E_{\frac{1}{2}}$rev.

Figure 28. Half Wave Potential vs Water Concentration for HMIM Cl

b) *Mixture 2 Data.*

As with the HMIM Cl data we followed the same procedure with the mixture 2 sample. The

mixture 2 data has some similarities to the HMIM Cl samples with one exception of not having

an 8 M concentration of water. The sample of mixture 2 nominally containing 8 M of water

quickly separated into two phases. Figure 29 shows a single voltammogram of Cu (II) in mixture

2 and its respective digital simulation. Just as in the measurements in HMIM Cl, the simulation

only slightly deviates from the experimental data. The lack of a clearly defined trend in the data

in Table 9 indicates that the differences between the kinetic data obtained for different scan rates

result only from a statistical error. Consequently, the data could be averaged, and the averages

are also listed in Table 9.   An inspection of the averaged data for various water contents

revealed an influence of water on the kinetic parameters of the Cu (II)/Cu (I) system. Figure.30

shows an effect of water on the rate constant of the reaction. The effect is similar to that

observed for HMIM Cl, i.e., the rate constant is increasing with an increasing water

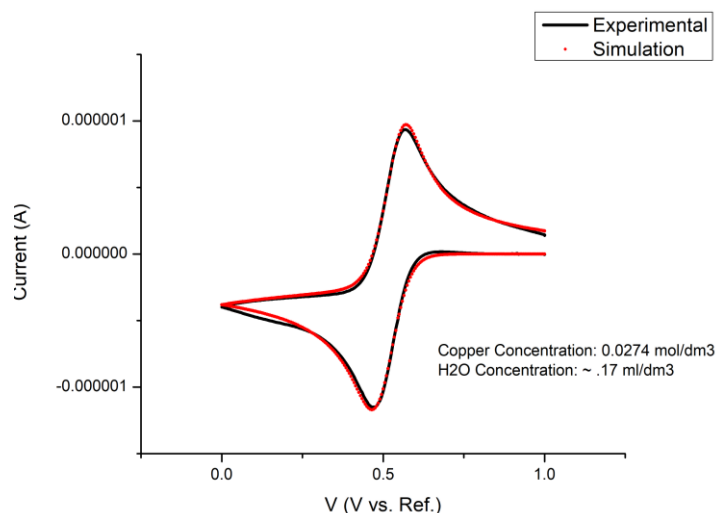concentration, except the magnitude of the effect is smaller than that observed for HMIM Cl.

Figure 29. 20mV/s Scan of Mixture 2

Table 9. All Simulations Parameters for HMIM Cl with 0.0274 mol/dm^3 of CuCl$_2$ with .1682 mol/dm^3 of water

Scan Rate	Ir	E*	α	k_s	Cu(II)	Cu(I)
mv/s	Ω	v		cm/s	cm^2/s	cm^2/s
20	5000	0.52069	0.41317	1.79E-04	5.21E-08	5.21E-08
50	5000	0.52003	0.46813	2.14E-04	4.80E-08	4.80E-08
100	5000	0.52049	0.47869	2.49E-04	5.40E-08	5.40E-08
200	5000	0.52098	0.45999	2.75E-04	5.70E-08	5.70E-08
500	5000	0.52178	0.46568	2.88E-04	5.70E-08	5.70E-08
750	5000	0.52252	0.4682	2.90E-04	2.90E-08	2.90E-08
20	5000	0.52125	0.47464	1.94E-04	6.90E-08	6.90E-08
Avg		5.21E-01	4.61E-01	2.41E-04	5.23E-08	5.23E-08
std dv		7.75E-04	2.04E-02	4.25E-05	1.13E-08	1.13E-08
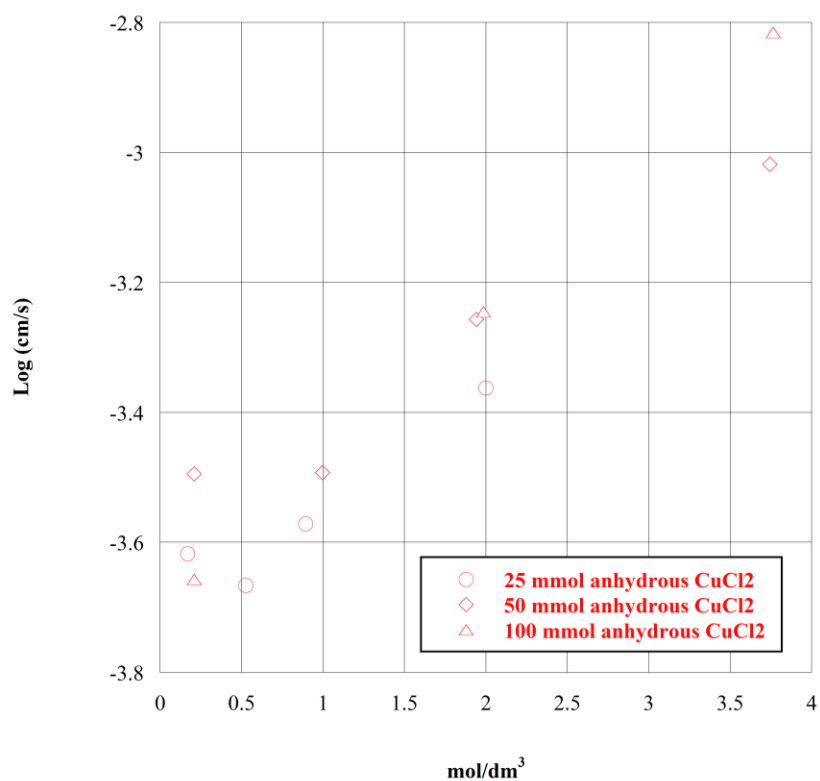
Figure 30. Average k_s vs Water Concentration for Mixture 2
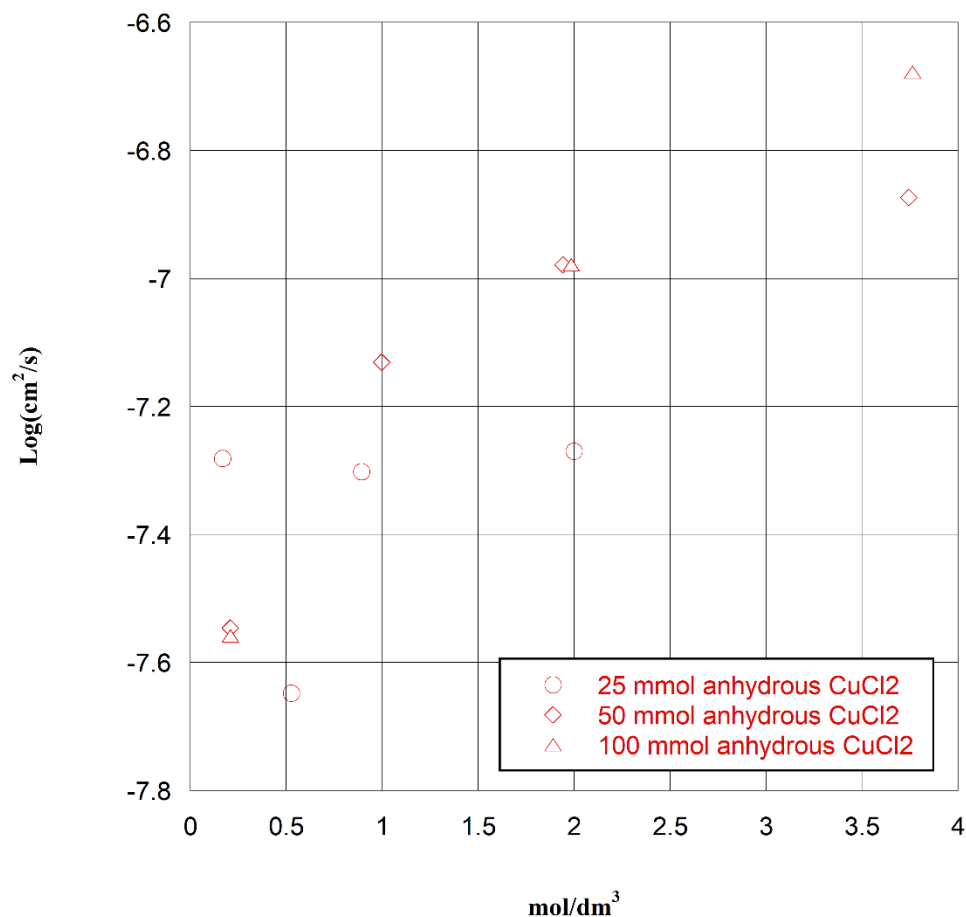
Figure 31. Average Diffusion Coefficient vs Water Concentration for Mixture 2

As in HMIM Cl, the diffusion coefficients in mixture 2, Figure 31, were found to increase with the water content. However, the increase is smaller than that observed for HMIM Cl (Figure 26). The transfer coefficient decreases with the water content in the mixture, Figure 32. This suggests that the transition state is becoming progressively closer to the initial Cu (II) state when the water content is increasing. For mixture two, the $E_{\frac{1}{2}}$ vs water concentration, Figure 33, the dependence seems to be dominated by changes in liquid junction potential.
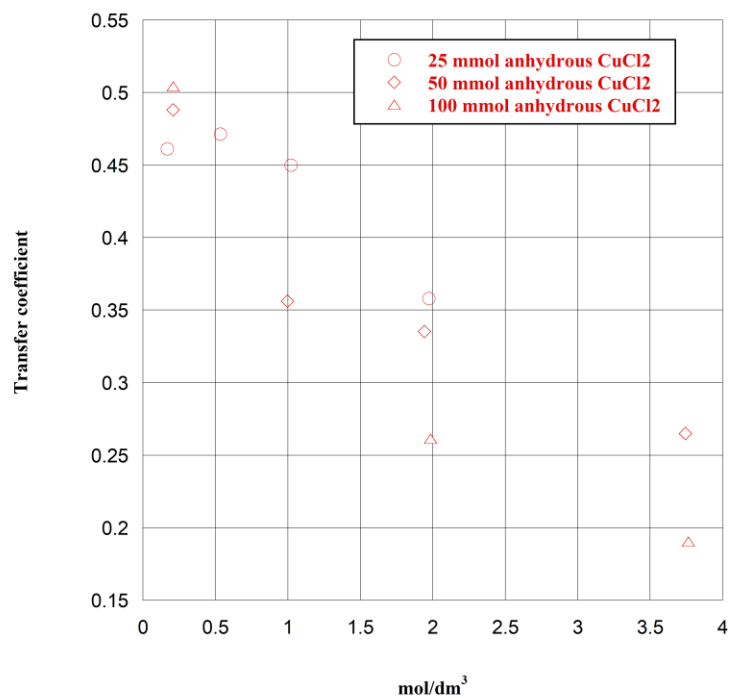
Figure 32. Transfer Coefficient vs Water Concentration for Mixture 2
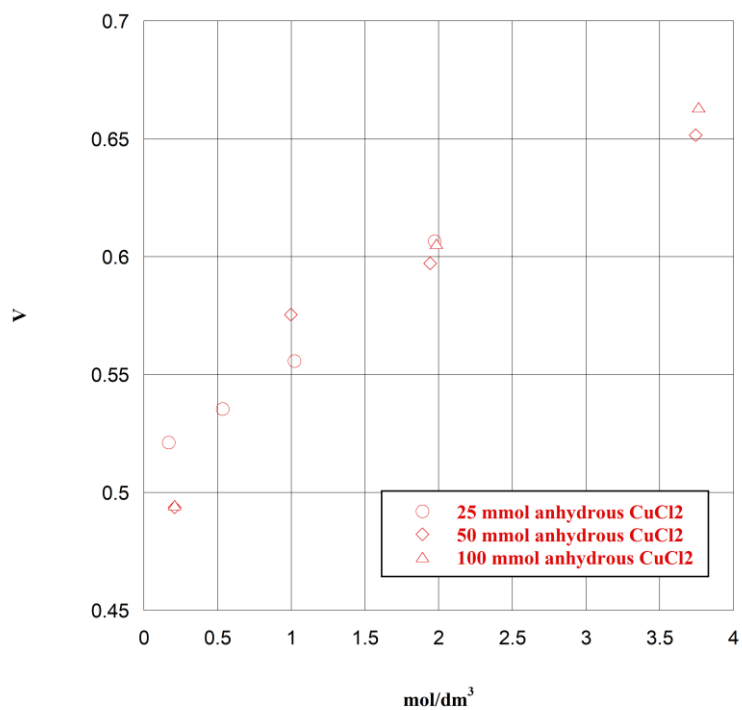
Figure 33. Half Wave Potential vs Water Concentration for Mixture 2

2. Material Characterization module

a) *HMIM Cl Data.*

A visual inspection of the 2D scattering images (SAXS, Figure 34 and WAXS, Figure 35), reveals the presence of periodic (X-ray scattering) morphological features in the studied HMIM Cl + CuCl$_2$ + H$_2$O solution.
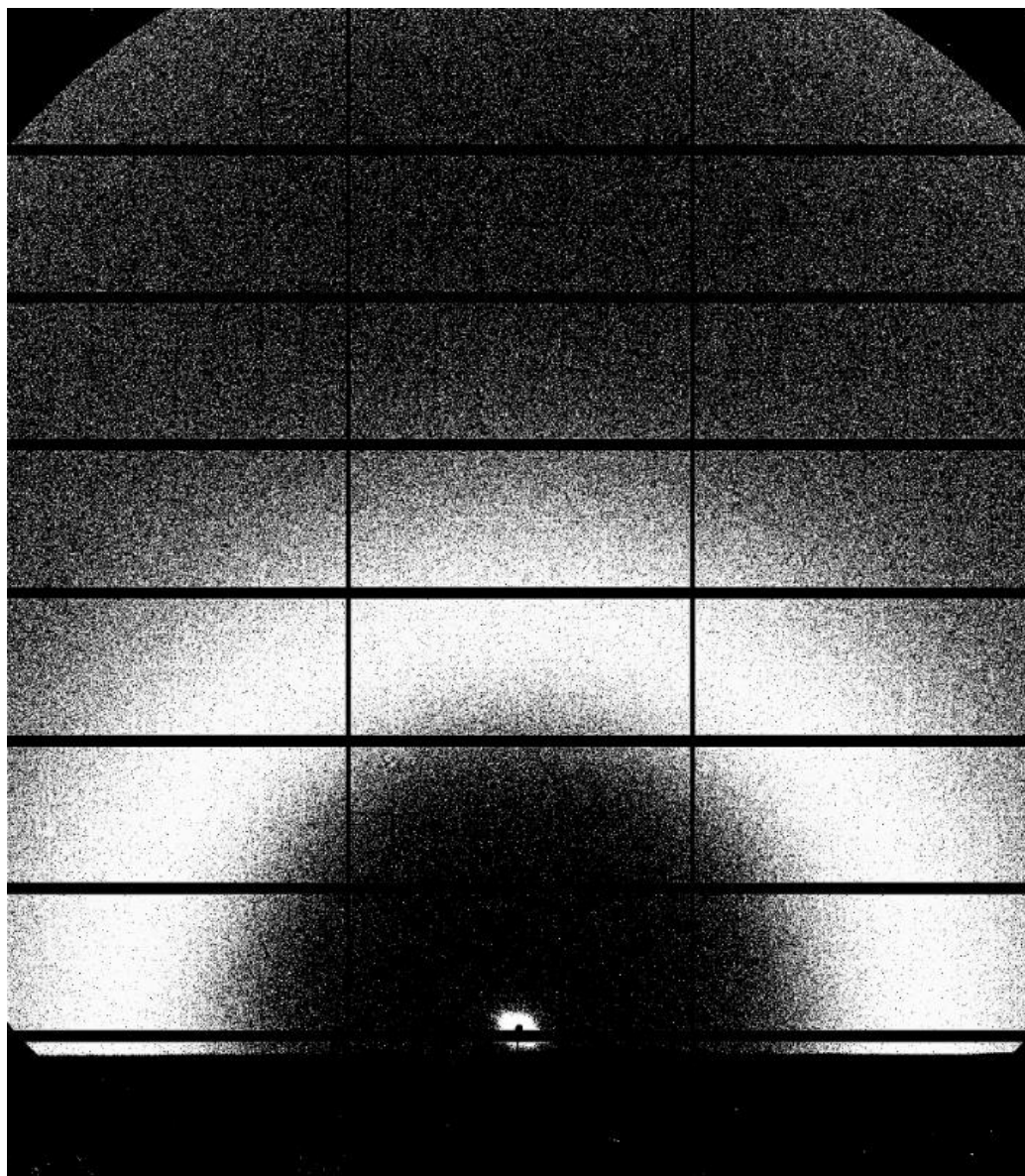
Figure 34. 2D SAXS Image of HMIM Cl with 25 mmol dm^{-3} of CuCl$_2$ with a Cu(II) to Water Molar Ratio of 20 to 1
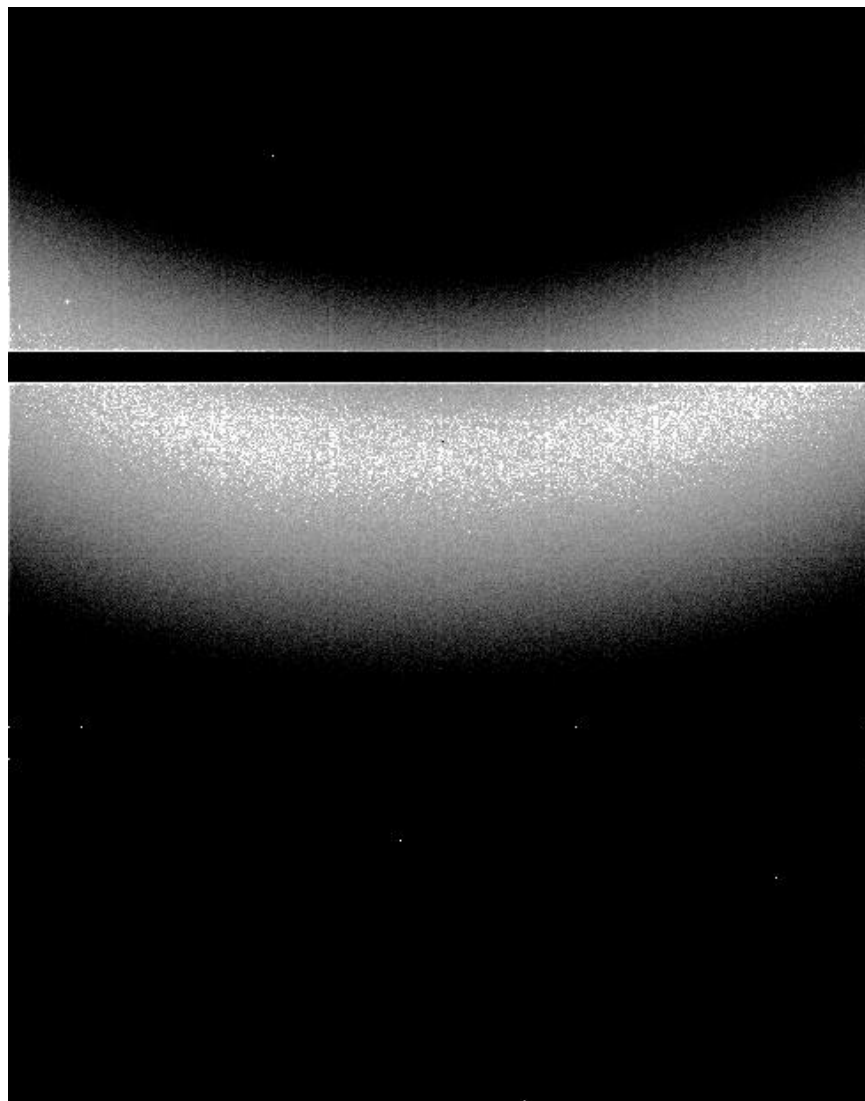
Figure 35. 2D WAXS Image of HMIM Cl with 25 mmol dm^{-3} of CuCl$_2$ with a Cu(II) to Water Molar Ratio of 20 to 1

Those features can be further characterized from the respective 1D image, Figure 36. A broad peak at 0.33 Å^{-1} and a very small bump near 0.99 Å^{-1} can be tentatively assigned to a 50/50 lamellar structure with d-spacing ≈ 19 nm. There is also a broad peak around 1.55 Å^{-1}, which we currently attribute to water. The SAXS analysis is unable to ascertain if copper plays a

role in the structure. The presence of either water or Cu (II) in HMIM Cl (Figure 37) does not

seem to affect the structure. More analysis is needed to ascertain if water or copper effects the

number of structures seen in the samples.
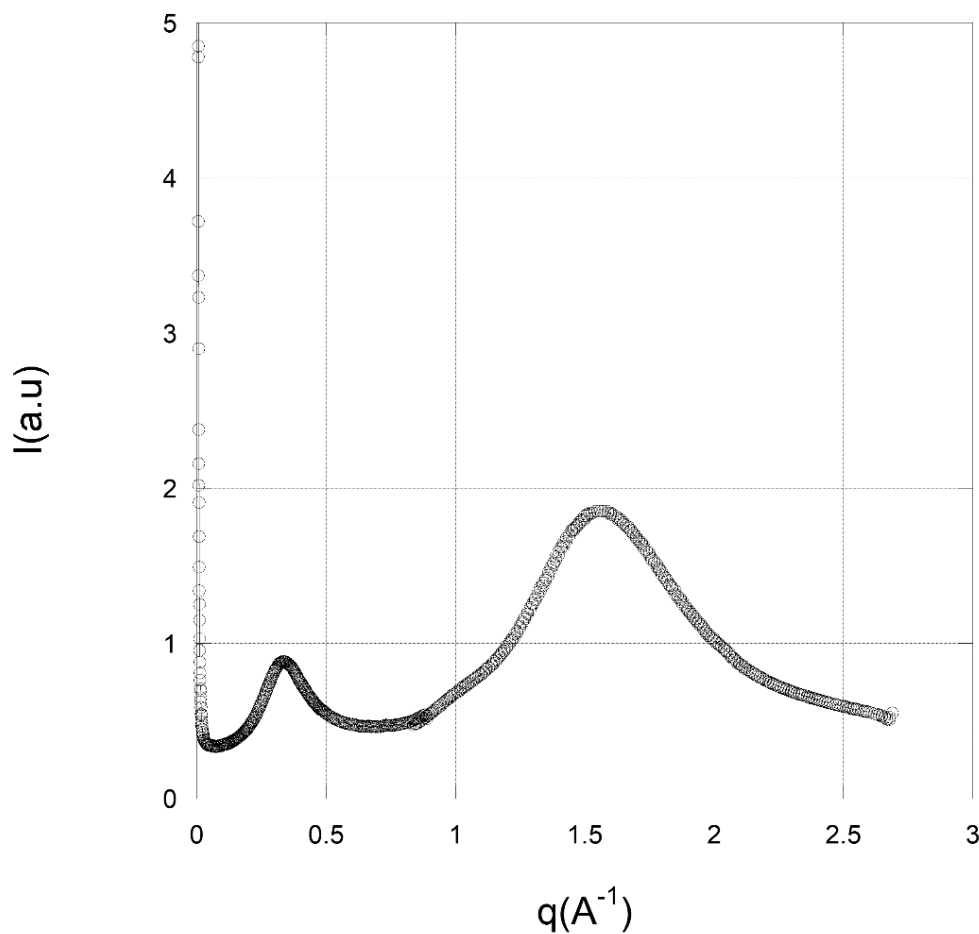
Figure 36. 1D SAXS Image of HMIM Cl with 25 mmol $CuCl_2$ with a Cu(II) to Water Molar Ratio of 20 to 1
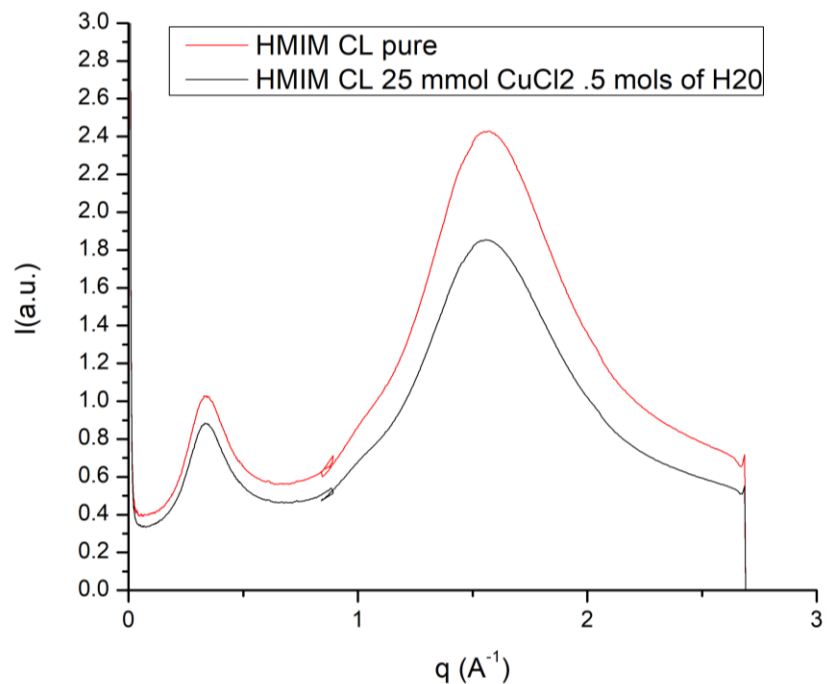
Figure 37. Comparison of 1D SAXS Images of HMIM Cl

b) *Mixture 2 Data.*

A visual inspection of the 2D scattering images (SAXS, Figure 38 and WAXS, Figure

39), reveals the presence of periodic (X-ray scattering) morphological features in the studied

Mixture 2 + $CuCl_2$ + H_2O solution.
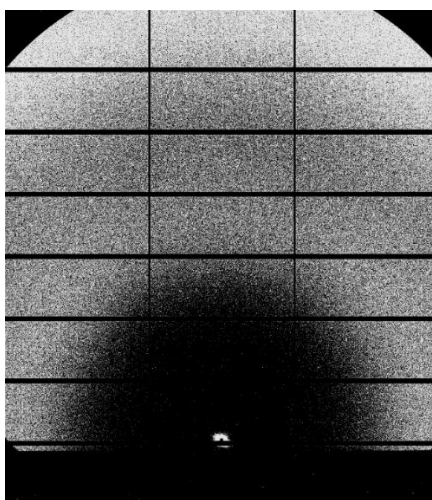
Figure 38. 2D SAXS Image of Mixture 2 with 25 mmol of $CuCl_2$ with a Cu(II) to Water Molar Ratio of 20 to 1

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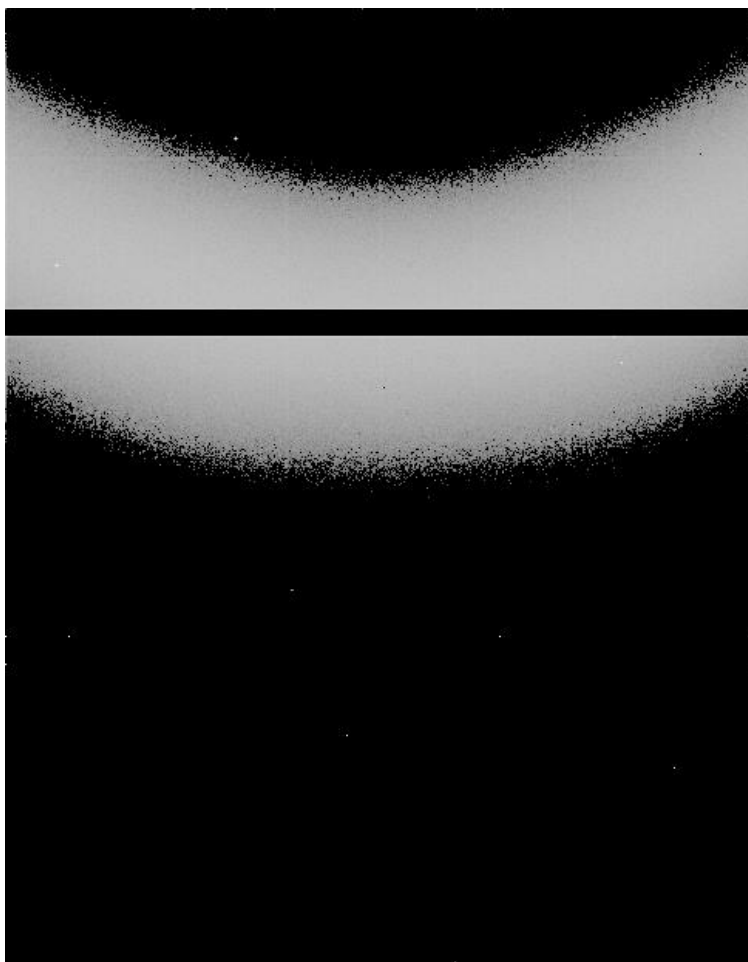
Figure 39. 2D WAXS Image of Mixture 2 with 25 mmol of CuCl$_2$ with a Cu(II) to Water Molar Ratio of 20 to 1

In similarity to HMIM Cl, mixture 2 was found to scatter X-rays, which indicated the presence of periodic morphological features in the liquid. The weak peaks at 0.42 Å^{-1} and 0.84 Å^{-1} in the 1D scattering graph (Figure 40) are tentatively assigned to a lamellar structure with d-spacing $\approx$ 15 nm. At q $\approx$1.40 Å^{-1} there appears to be a water peak. It appears at a somewhat different location in comparison to the HMIM Cl samples. Just as with the HMIM Cl sample it is not certain if copper plays a role in the structure. Moreover, the peaks resulting from the liquid morphology are unaffected by the presence of Cu (II) (Figure 41).
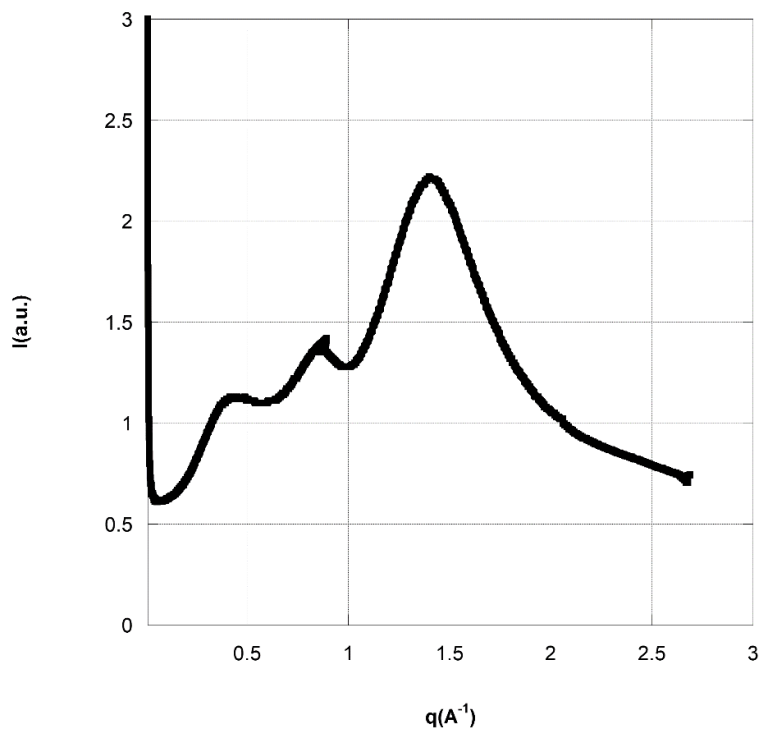
Figure 40. 1D SAXS Image of Mixture 2 with 25 mmol dm^{-3} of CuCl$_2$ with a Cu(II) to Water Molar Ratio of 20 to 1
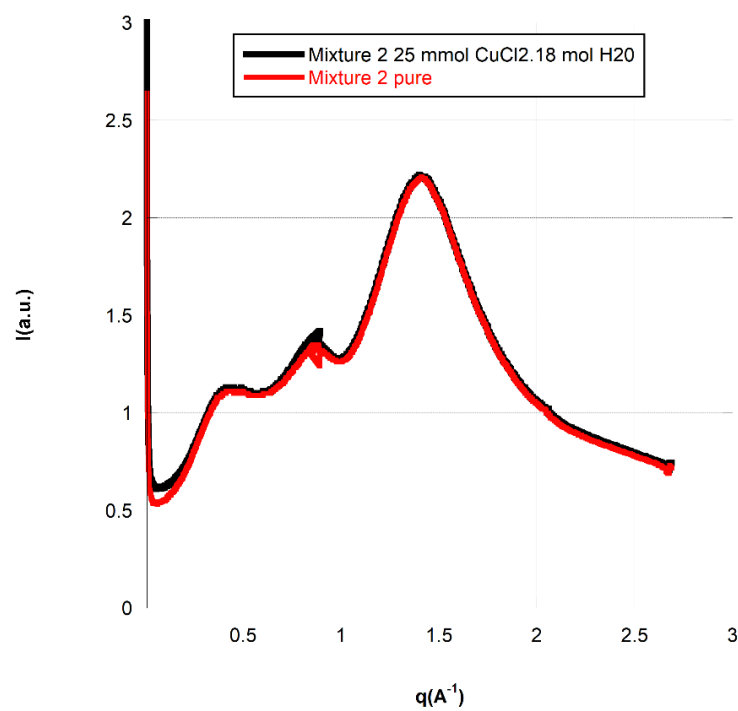
Figure 41. Comparison of 1D SAXS Images of Mixture 2

3. Computational module

a) Relaxation Failure.

This module failed in relaxing the structure. Normally, if the structure is relaxed one of the vectors in the stress tensor relaxes. Despite our best efforts, we couldn't get that to occur, Figure 42. The main reason is the structural complexity of HMIM Cl. According to the SAXS data, a one-dimensional structure forms in the liquid. It is unclear if the relaxation would ever recreate such a structure in the simulation as the starting point. The second reason is computational power. The system was created with the goal in mind of making sure anyone could use it. Therefore, not using super computing resources was important for the viability of the system. The complexity of the simulation suggests a lot of processing time for smaller systems. With a shared resource cluster used, trying to keep the processing time down proved difficult. It would take a very long time to relax the system on the small cluster used.
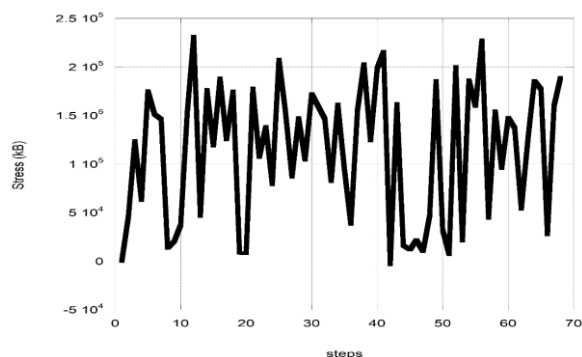
Figure 42. Stress vs Computational Steps

C. System Validation

Verification testing has shown that the test bed meets most of the technical specifications testing IL with solute. However, it fails to meet any specification involving the computational module. Connections between system requirements and sub-module verifications are presented in Table 10.

Table 10. System Requirements-Validations Connections

Sub-Module	System Requirements Validated	
Electrochemical Module	1.1	A manual shall be created to document procedural needs of utilization of the subsystem
	1.2	The manual shall facilitate directions for system operation and calibration techniques to anyone with standard lab training
	1.3	The system shall be physically adaptable to different test cells and electroanalytical techniques
	1.4	The system shall be physically adaptable to different test cells and electrochemical analytical techniques
	1.5	The system shall output current-potential data under cyclic voltametric conditions data at numerous scan rates within the range between 1 and 5000 mV/s
	1.9	The system will only be verified for criteria that fall within a 10% error of the expected value
Material Characterization module	1.7	The system shall output 1D X-ray scattering patterns
	1.9	The system will only be verified for criteria that fall within a 10% error of the expected value
Computational module	1.8	The system shall use Siesta to perform the molecular dynamics simulations

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Chapter 4: Utilization, Support, and Retirement Stage

A. System Operational, Maintenance, And Disposal

The operational, maintenance, and disposal stage is where analysis of the costs incurred by the operation and maintenance of the system throughout its lifecycle, as well as the specific procedures required.

1. System Operation

The electrochemical module operates under safety regulations set forth by Los Alamos National Laboratory. Therefore, the expectation is that I will not go out of the scope of the work. The computational module operates under the network access and usage requirements established by Tennessee State University. The material characterization module will typically operate at a user facility. Since the user will not usually be responsible for the operation, its operation will not be discussed here. Each subsystem is independent of each other, and the order is insignificant. The systems expected operation is indefinite as swapping out components as they wear out since most parts are durable if they are used as intended or upgraded as needed.

2. System Maintenance

The systems engineering process looks at the entire process of a system from beginning to end. While often overlooked maintenance and support are integral to the design process. These plans must be integrated into the planning during the conceptual design phase and developed as during the systems process. Maintenance is broken down by who performs the maintenance. Maintenance can be performed on the organizational, intermediate, or manufacturer/depot/supplier

level. For the proposed system maintenance is at the organizational level. Organizational Maintenance

Organizational maintenance can be defined as on-site corrective and preventive maintenance. The following sections explain the corrective and preventive maintenance that will be the responsibility of the organization.

a) Corrective Maintenance.

Corrective maintenance is defined as unscheduled maintenance performed to restore the system or product to a specified level of performance. For the proposed system, corrective maintenance will be performed in the following scenarios:

- Damaged or non-functioning analysis equipment

- Damaged or non-functioning computational resources

b) Preventive Maintenance.

Preventive maintenance is defined as scheduled maintenance performed to restore the system or product to a specified level of performance. For the proposed system, will be performed in the following scenarios:

- Potentiostat calibration on a yearly basis

- Server node replacement near expected end of life

3. System Disposal

All the hardware components of the system are recyclable if there's no damage, then there is no system disposal. Each piece of hardware can be used elsewhere. If any electronic piece of equipment is broken, it must be salvaged by the policies of Los Alamos National Laboratory or Tennessee State University. The ionic liquids with solute are disposed of according to organizational (LANL), state and federal regulations.

B. Life Cycle Costs

Life cycle cost (LCC) is the total cost involved in planning, design, construction, operation, maintenance, and the replacement/disposal of the entire system. The costs required for building the system, maintenance cost, initial cost and other cost are summarized this section. The associated costs with the system not including the personnel costs can be found in Table 11 with total of $49,600. There is one variable cost which is not included in the table and that is the cost of a beam time at the Advanced Photon Source at Argonne National Laboratory. This is because for non-proprietary work published in the open literature, beam time is free; for proprietary work, users must pay the APS an hourly fee for operational costs. This project involves no-proprietary work, and the hourly cost is irrelevant. In addition to the associated expenses detailed in Table 12, the life-cycle costs of the system include the average salaries of the personnel required for technical expertise in the development of the system, namely the Electrochemist, Computational Chemist and a Material Scientist. That cost is $300,000 for a year. The total cost on average for the system is $349,600.

Table 11. Average Cost of Materials for the System

Item	Cost
Potentiostat	$9000
Computer resources for potentiostat	$500
Ionic liquids	$1300
Electrodes	$500
Reference electrode parts	$300
Lab supplies	$1000
Server nodes	$27000
Management and network infrastructure	$10000

Table 12. Average Cost for Personnel for a Year

Personnel	Salary
Electrochemist	$100000
Computational Chemist	$100000
Material Scientist	$100000

Chapter 5: Conclusions and Recommendations

A. Conclusions

Based on the outcomes and evaluations of tests performed by the RTIL testbed, it is possible to investigate the RTIL's morphology and chemical properties' impact on the electron transfer processes of simple inorganic ions. Even though one of the modules failed, the system was designed in such a way that if two of the three modules worked then the research goal could be met. This is in part due to the material characterization module being dependent on getting a proposal accepted by APS. It is fortunate for this project that the customer had a relationship with APS that allowed a quick turnaround. Though it needs to be said that it is still a goal to complete the computational module as that module could give information on the structure of the 1-dimensional layer seen in the material characterization module as well as that of the structure of copper chloride in the RTIL's.

Using the RTIL testbed one can see that there is a dependence on the water concentration of the charge transfer kinetics and diffusion coefficient of Cu (II) in these particular RTILs. This is due to a change in the viscosity of the RTIL determined by computational and experimental methods, which will be recommended as an added test to the material characterization module. The RTIL testbed also shows us that the chosen RTILs have the same structure regardless of the water and copper concentrations. This indicates that the bulk structure of the RTIL does not affect the electron transfer processes in a significant way as previously thought by the customer. It is still unknown how RTIL structure at the electrode surface affects electron transfer.

B. Recommendations

Once the system was tested it was found that each module and even the input to the system has several areas of improvement that could make the system better. It is important to note that these recommendations are based on the test IL. There might be more optimal recommendations based on the IL selected.

1. Sample recommendations

One of the major sources of error when examining the electrochemical data can be linked to the accuracy of the weights of the components of the samples. To conserve IL creating small samples was the preferred method. This meant that the mass of copper chloride in the samples were no more than .5 g. With such a small amount being weighed and transferred to a bottle there was some error. If the user uses a larger sample, the measurement errors can be reduced. Though with this recommendation the user must make sure that the sample is mixed thoroughly to ensure sample homogeneity.

It was also found that when selecting a solute, it would be best to select solutes corresponding to all reagents participating in the redox reaction. In this document, copper (II) chloride was chosen as the solute. In that compound, copper is in a +2 oxidation state. Upon reduction, Cu (II) becomes Cu (I), i.e., it is in a +1 oxidation state. Electrochemical experiments can be performed on samples of CuCl where Cu is in a +1 oxidation state and could be included as supplementary information for the data gathered from the electrochemical module. This will allow for a more accurate determination of the effects of the liquid viscosity on the charge transfer kinetics and the diffusion coefficients.

2. **Temperature controlled experiments**

The following recommendation of performing temperature-controlled experiments can be applied to all of the modules. Since it was found that water content and therefore viscosity affects the kinetics of the IL/solute it stands to reason that increasing the temperature would have a similar effect. Each module can be modified easily to accomplish this.

3. **Electrochemistry module recommendation**

During the experiments performed in this module it was found that the external environment (temperature, humidity, etc.) may affect the electrochemical properties of the studied reaction in ILs. Consequently, the first recommendation is to use an environmental chamber that will allow the user to have a static environment. The user can then control the temperature and humidity in that chamber. All experiments can be improved on the techniques and equipment used. The following list summarizes possible improvements the techniques and equipment that can be applied to improve the module.

- Using a double chambered reference electrode for a more reproducible reference potential.

- Water content in the reference electrode solutions is adjusted to match the sample's water content.

- A sealed cell that would keep water out and ensure that the entire cell if heated has no temperature gradients.

- Adding different electrochemistry techniques to module to improve accuracy of the determination of the charge transfer kinetics.

4. Material characterization module recommendation

With the conclusion of water content and therefore viscosity affecting the kinetics the first recommendation is performing sample viscosity measurements or gathering the relevant data from literature. The physical measurements might pose a problem as some IL are very viscous and may require specialized equipment that some smaller labs might not have access to. The last recommendation is to add more spectroscopic measurements such as UV-VIS and Raman to try characterize the complexes formed by the solute.

5. Computational method

As stated in the System Verification section the system was created with the goal in mind of making sure anyone could use it. Therefore, not using super computing resources was important for the viability of the system. This was an underestimation of the complexity of the problem. This system is very complex and needs a large model to correctly model the complexity of the IL, the coordination sphere of Cu (II), and the location of the water in the system. Therefore, it is recommended to use a supercomputer for performing the simulation of the IL /solute system.

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